INORGANIC CHEMISTRY.

INORGANIC CHEMISTRY,

BY

EDWARD FRANKLAND, PH.D., D.C.L., LL.D., F.R.S.,

PROFESSOR OF CHEMISTRY IN THE NORMAL SCHOOL OF SCIENCE, LONDON,

AND

FRANCIS R. JAPP, M.A., PH.D., F.I.C.,

ASSISTANT PROFESSOR OF CHEMISTRY IN THE NORMAL SCHOOL OF SCIENCE, LONDON.

WITH 51 ILLUSTRATIONS AND A PLATE.

PROSUNT QUAE OMNIBUS

PHILADELPHIA:

LEA BROTHERS & CO.

1885.

PREFACE.

The Lecture Notes for Chemical Students, already published by one of us and now in their third edition, were always intended to be the precursors of text-books on Mineral and Organic Chemistry. The present volume fulfils this intention so far as Inorganic Chemistry is concerned. It is constructed on those principles of Classification, Nomenclature, and Notation which, after an experience of nearly twenty years, have been found to lead most readily to the acquisition of a sound and accurate knowledge of elementary chemistry.

In the Introduction we have endeavored to present to the student a connected account of the chief chemical theories at present prevailing, introducing only so much descriptive matter as is necessary for the elucidation of the subject. Afterwards, in the descriptive part of the work, the necessary references to the theoretical portion are given. In some of the theoretical sections, we have followed modes of treatment adopted by H. Kopp, Lothar Meyer, and Naumann in their well-known works. We have also to express our obligations to Fittig's excellent "Grundiss der unorganischen Chemie."

Although it would be out of place, in an elementary work like the present, to impart detailed instruction in the technical applications of chemistry, we have not hesitated to give brief outlines of some of the more important of these applications.

Normal School of Science and
Royal School of Mines,
South Kensington, London.
September, 1884.

TABLE OF CONTENTS.

INTRODUCTION.

CHAPTER I.

MATTER AND FORCE.

CHAPTER II.

ELEMENTS AND COMPOUNDS.

CHAPTER III.

CHEMICAL NOMENCLATURE.

CHAPTER IV.

LAWS OF COMBINATION.

CHAPTER V.

THE ATOMIC THEORY.

CHAPTER VI.

MOLECULAR WEIGHTS.

CHAPTER VII.

ATOMIC WEIGHTS.

CHAPTER VIII.

CHEMICAL NOTATION. ATOMICITY.

CHAPTER IX.

COMPOUND RADICALS.

CHAPTER X.

CLASSIFICATION OF ELEMENTS.

CHAPTER XI.

RELATIONS BETWEEN CHEMICAL COMPOSITION AND SPECIFIC GRAVITY. ATOMIC VOLUME.

CHAPTER XII.

CHEMICAL AFFINITY.

CHAPTER XIII.

CHEMICAL HOMOGENEITY.

CHAPTER XIV.

ISOMERISM, METAMERISM, POLYMERISM, ALLOTROPY.

CHAPTER XV.

HEAT OF CHEMICAL COMBINATION.—THERMOCHEMISTRY.

CHAPTER XVI.

FUSION AND FUSING-POINTS.

CHAPTER XVII.

EBULLITION AND BOILING-POINTS.

CHAPTER XVIII.

SOLUTION.

CHAPTER XIX.

DIFFUSION.

CHAPTER XX.

CRYSTALLOGRAPHY.

CHAPTER XXI.

WEIGHTS AND MEASURES.

NON-METALS.

CHAPTER XXII.

MONAD ELEMENTS.

CHAPTER XXIII.

DYAD ELEMENTS.

CHAPTER XXIV.

TRIAD ELEMENTS.

CHAPTER XXV.

TETRAD ELEMENTS.

CHAPTER XXVI.

PENTAD ELEMENTS.

CHAPTER XXVII.

HEXAD ELEMENTS.

CHAPTER XXVIII.

MONAD ELEMENTS.

CHAPTER XXIX.

TETRAD ELEMENTS.

CHAPTER XXX.

PENTAD ELEMENTS.

METALS.

CHAPTER XXXI.

DISTINGUISHING CHARACTERISTICS OF THE METALLIC ELEMENTS.

CHAPTER XXXII.

MONAD ELEMENTS.

CHAPTER XXXIII.

DYAD ELEMENTS.

CHAPTER XXXIV.

DYAD ELEMENTS.

CHAPTER XXXV.

TRIAD ELEMENTS.

CHAPTER XXXVI.

TETRAD ELEMENTS.

CHAPTER XXXVII.

METALS OF THE RARE EARTHS.—TETRAD ELEMENTS.

PENTAD ELEMENTS.

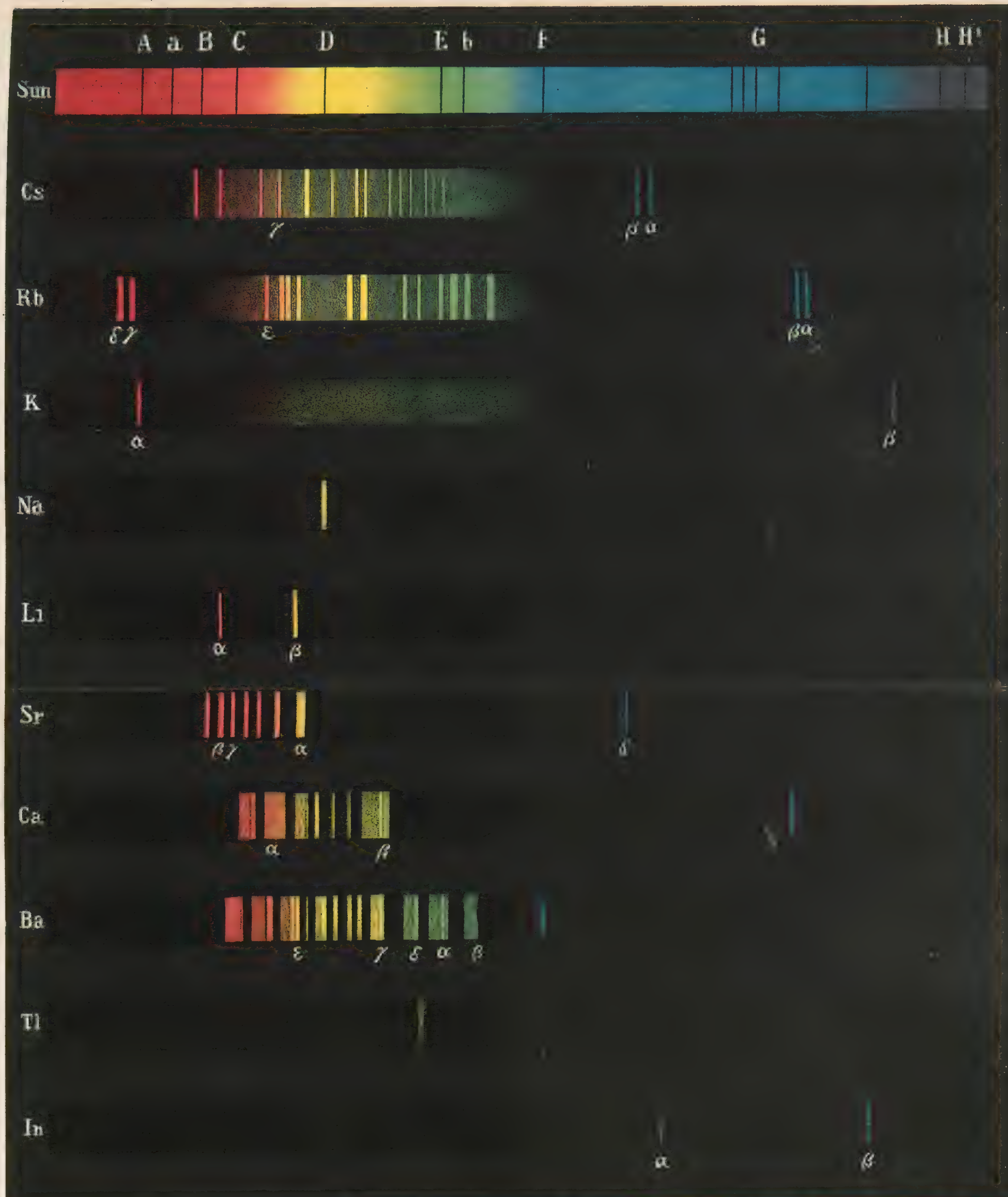
TRIAD ELEMENTS.

CHAPTER XXXVIII.

TETRAD ELEMENTS.

CHAPTER XLI.

HEXAD ELEMENTS.



A a B C D E b F G H H'
Sun
Cs
Rb
K
Na
Li
Sr
Ca
Ba
Tl
In

INORGANIC CHEMISTRY.

CHAPTER I.

MATTER AND FORCE.

In the most cursory observation of the objects surrounding us, our attention is arrested by two things—matter and motion. We see clouds drifting over our heads and rain falling from these clouds. The descending water flows in river beds or plunges in cataracts down precipices, making its way in both cases to the sea. The surface of that sea is in constant motion, whilst ships driven by wind or steam make their way through its waters. On land, animal life everywhere exhibits matter in motion. The air is rarely still, and many of the heavenly bodies are constantly changing their places in the sky. All this we cannot help observing; a somewhat more minute examination, however, shows us that matter not only thus suffers a change of place, but that it also frequently undergoes other changes. Thus water becomes ice or steam, iron rusts, coal burns, and certain substances such as glass and sealing-wax acquire, when rubbed, the property of attracting light bodies.

Now this motion of matter and these changes which matter undergoes are all brought about by what is termed *force.* This force assumes several different forms, which are sometimes regarded and generally described as distinct forces: thus the transformation of water into ice and steam is due to the operation of two of these forces which act antagonistically to each other, and are termed *cohesion* and *heat;* the rusting of iron and the burning of coal are brought about by *chemical force;* the impression produced upon the eye by the combustion of coal is due to *light;* the attractive power of the glass and sealing-wax is the effect of the *electric force;* whilst the motion of the heavenly bodies and that of water from the clouds to the sea are the result of the action of a force called *gravity.*

The department of knowledge which deals with these phenomena is termed Natural Science.

Natural science studies and investigates the whole range of sensible objects. It teaches us the properties of these objects and the various changes which they undergo, either in the ordinary course of nature or by the application of extraordinary and arti-

ficial means. This vast field of observation and research has been divided into two great sections, viz.:

1. Statical sciences.
2. Dynamical sciences.

The statical sciences study objects in a state of rest with reference to their form, magnitude, situation, structure, and other properties; such branches of science are Descriptive Astronomy and Geology, Mineralogy, Botany, Zoology, Animal and Vegetable Anatomy.

The dynamical sciences take into consideration the changes to which sensible objects are subject. They are subdivided into two groups. The first group studies these changes without reference to their causes: such are Physical Astronomy and Geology, and Animal and Vegetable Physiology. The second group investigates the changes which bodies undergo with special reference to the causes of such changes. These are Physics and Chemistry. This classification of the natural sciences, however, must not be taken in too strict a sense, especially in the case of the second section, for the astronomer and geologist are nowadays rarely content to observe changes without inquiring into their causes: the same is still more frequently the case with the physiologist, and thus physics and chemistry are continually appealed to in the development of astronomy, geology, and physiology.

The force to which the phenomena of chemistry are primarily ascribed, and which is commonly termed *chemical affinity*, is therefore closely associated with the other great forces of nature, but it is sharply distinguished from them, in the first place, by producing permanent changes in the properties of the bodies subject to its action. The other forces do not permanently alter the properties of matter, but when substances are brought under the influence of chemical force, they are scarcely if at all afterwards recognizable by the unaided senses. The presence of the bright, hard, colorless and heavy metal iron, could not even be suspected in the dull, soft, brown, and comparatively light rust, into which it is converted by exposure to the air; still less, perhaps, could the rust be credited with the presence of the colorless and invisible gas, oxygen, which is held in combination with the iron by chemical energy. The change is such as is not produced by mixture only. Mechanical mixture, however intimate, does not conceal the properties of iron and sulphur, for instance. The magnetic quality of the iron is as marked as ever, and the two constituents may be distinguished and even separated from each other under the microscope. But after these substances have been subjected to chemical action, the most powerful microscope is incompetent to detect either sulphur or iron, and the magnetic property of the metal almost entirely disappears. This change of properties is manifested in various ways: sometimes liquids or gases are converted into solids, or *vice versâ*, sometimes a change in color, taste, odor, or medicinal pro-

perties is produced, and there is always a change of temperature, sometimes in the direction of heat, and sometimes in that of cold. With all these changes, however, there is never the slightest alteration in the weight of the materials operated upon.

In the second place, chemical affinity cannot act through an appreciable intervening space. Heat, light, and electricity affect bodies at considerable distances, whilst gravity acts through spaces inconceivably great; but if two substances, between which the chemical force is energetically exerted when they are in contact, be placed at the smallest appreciable distance from each other, no chemical action whatever occurs, even after they have been in close proximity for years. Of all other forces, cohesion alone requires this intimate contact. If two pieces of plate glass be gently placed one upon the other, the slightest effort suffices to separate them, but if they be pressed together, they markedly cohere, and if strongly pressed for a long time, they can no longer be separated. The two pieces have become one by cohesion, but the properties of the glass are unaltered, and cohesive action is thus sharply distinguished from chemical action.

The most distinguishing characteristic of the chemical force, however, is the limitation of its action to fixed and definite quantities of matter. Each chemical compound not only always contains the same kinds of matter, but its constituents are always present in exactly the same proportions, although the specimens of the compound may have been derived from the most widely different sources. Thus water obtained from melting snow, from rain, from steam or from the artificial combination of its constituents, always consists of oxygen and hydrogen in the proportion of one part by weight of the latter to eight parts of the former. Again, common salt, whether obtained naturally from the mines of Cheshire or Poland, from the brine springs of Germany or America, from the salt lakes of Russia or Australia, from sea water, or prepared artificially from its constituents, always consists of chlorine and sodium in the proportion of 35.5 parts of the former to 23 parts of the latter. *When two bodies combine chemically or become united together by the chemical force, they do so in fixed and definite proportions.*

The materials composing our universe are bound together by a force which, whether regarded as attraction or as pressure, produces three sets of phenomena differing so much from each other as to lead to their being commonly referred to three of the distinct forces already mentioned. One of these is gravitation, which acts through distances inconceivably great. The second is cohesion, which acts only through spaces too small to be measured. The third is chemical attraction or chemical affinity which, like cohesion, also acts through distances too small to be measured, but which, as already mentioned, is distinguished, both from gravitation and cohesion, by producing a change of properties in the matter upon which it acts.

Thus a lump of ice presses towards the centre of the earth,

being pulled in that direction by the attraction of gravitation, which can be overcome by mechanical means.

The lump of ice is made up of smaller pieces, for it can be broken up into an immense number of particles by mere mechanical effort, and thus cohesive attraction, like gravity, is overcome by mechanical means; but only partially, for each particle is made up of smaller particles still bound together by the same force.

If, however, heat be applied to the ice, another well-marked step in the conquest of cohesion is gained, and *liquidity* is induced—a condition in which the particles of the water move freely about and amongst each other. But even here cohesion is not completely vanquished, and the particles still cling to each other with a considerable amount of tenacity. By the application of a greater amount of heat, the complete conquest of cohesion is at last achieved. In the condition of steam, the particles of water no longer stick together: they are entirely freed from all cohesive force, and are only restrained from flying asunder to infinite distances by gravitation and external impediments.

In all these operations, the properties of the water have not been essentially or permanently altered. Even steam is, like water, uninflammable and incapable of supporting combustion. Moreover, on cooling, it is reconverted into water with all its properties unimpaired.

By heat, cohesion has thus been gradually but completely overcome, and the question now arises, can any further effect be produced upon water by the same agent? Experiment answers this question in the affirmitive, for if steam be subjected to the intense heat of a stream of electric sparks, it is resolved into a mixture of oxygen and hydrogen gases which refuses to condense to water on cooling, and which explodes by contact with flame. The properties of the steam have thus been entirely altered, and by this intense heat another remarkable step has been taken in the conquest of attractive force; each particle of steam has been broken up, and by the change of properties which has followed the rupture, the attraction overcome is recognized as that of chemical affinity.

The attractive forces thus operating within a mass of ice are enormous. They may be expressed in terms either of heat or of mechanical effort. In terms of heat ice requires as much heat to melt it, that is to convert it into liquid and ice-cold water, as would raise the temperature of an equal weight of water from 0° C. to 79.2° C. Water at 0° requires to convert it into steam as much heat as would raise its temperature to 637° C. if no steam were formed. But the separation of the oxygen from the hydrogen absorbs as much more heat as would raise the temperature of the steam to 10,315° C. if no separation occurred. In terms of mechanical effort the force required to convert 9 lbs. of ice into water is equal to that required to raise a weight of one ton to a height of 433 feet, to overcome the remaining cohesion and convert the water into steam requires a force sufficient to raise one ton to a height of 2,900 feet, whilst the power required for the separation

of the two constituents of steam would raise one ton a height of no less than 22,320 feet.

CHAPTER II.

ELEMENTS AND COMPOUNDS.

ALL kinds of matter which we meet with on the earth may be divided into two classes, those which are capable of resolution into other simpler kinds of matter, and those which defy our attempts so to resolve them. The former are termed *compounds;* the latter, simple bodies or *elements.* For example, if red oxide of mercury be heated, the heat will exert, as in the case of steam already described, a disintegrating or decomposing action: the red oxide will break up into two substances—a colorless gas, oxygen; and a white heavy liquid, mercury. If the mercury and the oxygen be carefully weighed, it will be found that their weights are together exactly equal to that of the oxide of mercury employed; from which it may be concluded that none of the products of decomposition have escaped observation—that the liquid metal and the colorless gas, and nothing beyond these, went to make up the red powder. This opinion is confirmed by the fact that it is possible, under suitable conditions, to reproduce the red powder from oxygen and mercury. The process of resolving a compound into its constituents is known as *analysis;* that of building it up from its constituents is termed *synthesis.*

Red oxide of mercury is therefore a compound, and its components are mercury and oxygen. Can these components be resolved into still simpler bodies?

The answer is, the resources of chemical science have not as yet been able to effect any such resolution. Both mercury and oxygen may be brought into union with various other bodies, and may be led by complicated processes from one combination to another; but at the end of their course they always emerge unchanged, and, if they do possess constituents, none of these have been dropped by the way. As no other kinds of matter can be extracted from them, it is agreed to regard them as *elements.*

It is quite possible that the elements merely denote the present limits to our powers of effecting chemical decomposition. The only criterion which we have of the elementary nature of a body is, as above stated, the purely negative one of our inability to decompose it; and the history of the science shows us that this criterion is not necessarily trustworthy.

The following is a list of the seventy elements at present recognized. The twenty-two most important of these are distinguished by the largest type, those next in importance by medium type, whilst the names of elements which are either of rare occur-

rence, or of which our knowledge is very imperfect, are printed in small type:

Name.	Symbol.*	Atomic weight.*	Name.	Symbol.	Atomic weight.
ALUMINIUM	Al	27	Nickel	Ni	58.6
Antimony	Sb	120	Niobium	Nb	94
Arsenic	As	75	NITROGEN	N	14
Barium	Ba	137	Norwegium	Ng	214
Beryllium	Be	9	Osmium	Os	198.6
Bismuth	Bi	208.2	OXYGEN	O	16
Boron	B	11	Palladium	Pd	105.7
BROMINE	Br	80	PHOSPHORUS	P	31
Cadmium	Cd	112	Platinum	Pt	194.4
Cæsium	Cs	133	POTASSIUM	K	39
CALCIUM	Ca	40	Rhodium	Rh	104
CARBON	C	12	Rubidium	Rb	85.3
Cerium	Ce	140.5	Ruthenium	Ru	104
CHLORINE	Cl	35.5	Samarium	Sm	150
Chromium	Cr	52	Scandium	Sc	44
Cobalt	Co	58.6	Selenium	Se	79
COPPER	Cu	63.2	SILICON	Si	28.2
Decipium	Dp	159	SILVER	Ag	107.7
Didymium	Di	146	SODIUM	Na	23
Erbium	Er	165.9	Strontium	Sr	87.5
FLUORINE	F	19	SULPHUR	S	32
Gallium	Ga	68.8	Tantalum	Ta	182
Gold	Au	196	Tellurium	Te	125
HYDROGEN	H	1	Terbium	Tb	148.8
Indium	In	113.4	Thallium	Tl	204
IODINE	I	127	Thorium	Th	233.4
Iridium	Ir	192.5	Tin	Sn	118
IRON	Fe	56	Titanium	Ti	48
Lanthanum	La	138.5	Tungsten	W	184
LEAD	Pb	206.5	Uranium	U	238.5
Lithium	Li	7	Vanadium	V	51.3
Magnesium	Mg	24.4	Ytterbium	Yb	172.8
MANGANESE	Mn	55	Yttrium	Y	89.8
MERCURY	Hg	200	ZINC	Zn	65.3
Molybdenum	Mo	95.5	Zirconium	Zr	90

It is usual to divide these elements into two great classes—*metals* and *non-metals*, the latter being sometimes also termed *metalloids*. The division is a somewhat arbitrary one, and the boundary-line between the two classes has been variously drawn by different chemists. Arsenic, selenium, and tellurium have been assigned to either category, according as the physical or the chemical characteristics formed the basis of the classification. Hydrogen, on the strength of its physical properties, is almost invariably classed as a non-metal; but its entire chemical behavior would lead to its being placed among the metals. An arrangement of the elements in their electro-chemical order, or a division into well-marked chemical groups, would perhaps be more logical.

* For an explanation see Chapter VIII.

CHAPTER III.

CHEMICAL NOMENCLATURE.

THE study of every science necessitates an acquaintance with the system of names and peculiar modes of expression which have been found most convenient to denote the materials and to describe the phenomena which form its objects. Such names and modes of expression constitute the groundwork of the language of every science, and upon the right employment of these depend the precision and accuracy of scientific definition.

The nomenclature of a science ought to be distinguished by clearness and simplicity; but it is by no means easy to secure these conditions in a science like chemistry, where the rapid progress of discovery necessitates the continual addition of new and the frequent alteration of old names. The chemical name of a substance should not only identify and individualize that substance, but it should also express the composition and constitution of the body, if a compound, to which it is applied. The first of these conditions is readily attained; but the second is much more difficult to secure, inasmuch as our ideas of the constitution of chemical compounds—of the mode in which they are built up as it were—require frequent modification. On this account all attempts to frame a perfectly consistent system of chemical nomenclature have hitherto been only partially successful.

The names of the elements can scarcely be said to have been given according to any rule; many of them are derived from some prominent property of the bodies themselves, whilst others have a mythological origin. An attempt has been made to distinguish the metals by the termination *um*, as potassium, sodium, etc.; but the common metals, such as gold, copper, and iron, still retain their original names; and one substance, selenium, which at the time of its discovery was regarded as a metal, has been suffered to retain its name unchanged, although further research has divested it of all metallic attributes. An important group of electro-negative* non-metals—flourine, chlorine, bromine, and iodine—have received the termination *ine;* three are distinguished by the terminal syllable *on*, viz., carbon, silicon, and boron; and three others have *gen* for their final syllable, viz., oxygen, hydrogen, and nitrogen, these last names being derived from Greek words denoting the property possessed by these elements of generating respectively acid, water, and nitre.

When two elementary bodies unite together, they form a chemical compound of the first order, to which the name *binary compound* has been applied. The names of these compounds are formed from those of their constituents, the name of the positive*

* See Electrolysis, Chapter XII.

constituent or some abbreviation thereof, with the termination *ic*, preceding that of the negative* constituent, which is made to terminate in *ide*, thus:

Potassium	and	Sulphur	form	Potassic sulphide.
Sodium	"	Oxygen	"	Sodic oxide.
Silver	"	Chlorine	"	Argentic chloride.
Zinc	"	Iodine	"	Zincic iodide.
Calcium	"	Chlorine	"	Calcic chloride.

But the same elements frequently form with each other two compounds, in which case the one which contains the smaller proportion of the negative element is distinguished by changing the terminal syllable of the name of its positive constituent into *ous*, the terminal *ic* being retained for the compound containing the larger proportion of the negative element. Thus:

One atom of tin and two atoms of chlorine form stannous chloride.
One atom of tin and four atoms of chlorine form stannic chloride.

Sometimes, however, the same elements form with each other more than two compounds. In these cases the prefixes *hypo* and *per* are employed as further marks of distinction; but their use is very rarely required.

If a binary compound contains oxygen, and forms an acid when made to unite with water, or a salt when added to a base, it is termed an *anhydride*. Thus:

One atom of carbon and two atoms of oxygen form carbonic anhydride.
Two atoms of nitrogen and five atoms of oxygen form nitric anhydride.
Two atoms of nitrogen and three atoms of oxygen form nitrous anhydride.
One atom of sulphur and three atoms of oxygen form sulphuric anhydride.
One atom of sulphur and two atoms of oxygen form sulphurous anhydride.

In the following cases, the systematic names have not displaced the trivial and irregular names used for the same substances:

Systematic name.	Trivial or irregular name.
Hydric oxide, ...	Water.
Hydric sulphide, . . .	Sulphuretted hydrogen.
Hydric selenide, . . .	Seleniuretted hydrogen.
Hydric telluride, . . .	Telluretted hydrogen.
Hydric chloride, . . .	Hydrochloric acid.
Hydric bromide, . . .	Hydrobromic acid.
Hydric iodide, . . .	Hydriodic acid.
Hydric fluoride, . . .	Hydrofluoric acid.
Hydric carbide, . . .	Marsh-gas or light carburetted hydrogen.
Hydric nitride, . . .	Ammonia.
Hydric phosphide, . .	Phosphoretted hydrogen.
Hydric arsenide, . . .	Arseniuretted hydrogen.
Hydric antimonide, . .	Antimoniuretted hydrogen.

The term *acid* was originally applied only to substances possess-

* See Electrolysis, Chapter XII.

ing a sour taste like vinegar; but analogy has necessitated the application of the same name to a large number of compounds which have not this property. In the modern acceptation of the name, an acid may be defined as a compound containing one or more atoms of hydrogen, which become displaced by a metal when the latter is presented to the compound in the form of a hydrate. The hydrogen capable of being so displaced may be conveniently termed *displaceable hydrogen.* An acid containing one such atom of hydrogen is said to be *monobasic,* one containing two such atoms *dibasic,* etc. Acids of a basicity greater than unity are frequently termed *polybasic acids.*

Thus nitric acid gives, with sodic hydrate, sodic nitrate:

$$\underset{\text{Nitric acid.}}{NO_3H} + \underset{\text{Sodic hydrate.}}{ONaH} = \underset{\text{Sodic nitrate.}}{NO_3Na} + \underset{\text{Water.}}{OH_2}.*$$

Sulphuric acid gives, with potassic hydrate, potassic sulphate:

$$\underset{\text{Sulphuric acid.}}{SO_4H_2} + \underset{\text{Potassic hydrate.}}{2OKH} = \underset{\text{Potassic sulphate.}}{SO_4K_2} + \underset{\text{Water.}}{2OH_2}.$$

And hydrochloric acid gives, with potassic hydrate, potassic chloride:

$$\underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Potassic hydrate.}}{OKH} = \underset{\text{Potassic chloride.}}{KCl} + \underset{\text{Water.}}{OH_2}.$$

When an acid contains oxygen, its name is generally formed by adding the terminal *ic* either to the name of the element with which the oxygen is united, or to an abbreviation of that name; thus sulphur forms, with oxygen, sulphuric acid; nitrogen, nitric acid; and phosphorus, phosphoric acid. But it frequently happens that the same element forms two acids with oxygen; and when this occurs, the acid containing the larger amount of oxygen receives the terminal syllable *ic,* whilst that containing less oxygen is made to end in *ous.* Thus we have sulphurous acid, nitrous acid, and phosphorous acid, each containing a smaller proportion of oxygen than that necessary to form respectively sulphuric, nitric, and phosphoric acids.

In some instances, however, the same element forms more than two acids with oxygen, in which case the two Greek words *hypo,* under, and *hyper,* over, are prefixed to the name of the acid. Thus an acid of sulphur containing less oxygen than sulphurous acid is termed hyposulphurous acid; and another acid of the same element containing, in proportion to sulphur, more oxygen than sulphurous acid and less than sulphuric, might be named either hypersulphurous acid, or hyposulphuric acid; but the latter term has been adopted. The prefix *per* is frequently substituted for *hyper;* thus in the case of chlorine, which forms the following four acids with oxygen, viz., hypochlorous acid, chlorous acid, chloric acid,

* For an explanation of these formulæ see Chapter VIII.

and hyperchloric acid, the latter is generally named perchloric acid; but *per* can only be used as a prefix to the acid containing the largest proportion of oxygen.

Some acids do not contain oxygen amongst their constituents, but consist of sulphur or hydrogen united with other elements. This peculiarity of composition is expressed in their nomenclature by the prefixes *sulpho* or *sulph* (or the equivalent Greek prefixes *thio* or *thi*), and *hydro* or *hydr:* thus sulpharsenic acid and sulphostannic acid denote acids composed respectively of sulphur, hydrogen, and arsenic; and sulphur, hydrogen, and tin; whilst the names hydrochloric acid and hydriodic acid are given to acids composed, the first of hydrogen and chlorine, and the second of hydrogen and iodine. The terminals *ous* and *ic* are also applied to these acids in exactly the same manner as to the oxygen acids; thus we have sulpharsenious and sulpharsenic acid, the latter containing a larger proportion of sulphur than the former; but the application of the first of these terminals has not hitherto been found necessary in the case of hydrogen acids, since no element has yet been observed to form more than one acid with hydrogen.

The term *anhydride* (cf. p. 40) is applied to the residue obtained by the abstraction (in combination with oxygen as water) of all the displaceable hydrogen from one or two molecules of an oxygen acid. Thus,

$$\underset{\text{Sulphuric acid.}}{SO_4H_2} \quad - \quad \underset{\text{Water.}}{OH_2} \quad = \quad \underset{\text{Sulphuric anhydride.}}{SO_3};$$

$$\underset{\text{Nitric acid.}}{2NO_3H} \quad - \quad \underset{\text{Water.}}{OH_2} \quad = \quad \underset{\text{Nitric anhydride.}}{N_2O_5}.$$

The term *anhydro-acid* or *pyro-acid* is applied to such acids as are formed from two molecules of a polybasic acid (see p. 41) by elimination of water:

$$\underset{\text{Phosphoric acid.}}{2PO_4H_3} \quad - \quad \underset{\text{Water.}}{OH_2} \quad = \quad \underset{\text{Pyrophosphoric acid.}}{P_2O_7H_4};$$

$$\underset{\text{Sulphuric acid.}}{2SO_4H_2} \quad - \quad \underset{\text{Water.}}{OH_2} \quad = \quad \underset{\substack{\text{Pyrosulphuric acid.} \\ \text{(Nordhausen sulphuric acid.)}}}{S_2O_7H_2}.$$

These acids are thus partial anhydrides. The prefix *pyro* originally referred to their mode of formation, heat being employed to drive off the water; but its use has been extended to acids which have been prepared by other means, and it is to be understood generally as denoting partial anhydricity between two molecules of the parent acid.*

* This sense of the prefix *pyro* must not be confounded with that in which it is employed in organic chemistry, as in *pyrotartaric acid*, *pyromucic acid*, *etc.* Here the mode of formation by the action of heat is alone indicated, the compounds having for the most part nothing further in common, and not being formed from the parent acid—*tartaric acid*, *mucic acid*—according to any fixed rule.

The term *base* is applied to three classes of compounds, all of which are converted into salts by the action of acids. These are:

1st. Certain compounds of metals with oxygen, such as sodic oxide (Na_2O), zincic oxide (ZnO), etc.

2d. Certain compounds of metals with the compound radical hydroxyl (HO), such as sodic hydrate ($Na(HO)$), zincic hydrate ($Zn(HO)_2$), etc.

3d. Certain compounds of nitrogen, phosphorus, arsenic, and antimony, such as ammonia (NH_3).

There are also a few organic compounds to which the name base is sometimes given, but which are not included in the above classes; it is, however, unnecessary further to allude to them here.

The bases of the first class are named in accordance with the rules already given for compounds of two elements. The following bases, however, still retain their irregular names:

Systematic names.	Irregular names.
Baric oxide, ...	Baryta.
Strontic oxide, ...	Strontia.
Calcic oxide, ...	Lime.
Magnesic oxide, ...	Magnesia.
Aluminic oxide, ...	Alumina.
Beryllic (Glucinic) oxide, . . .	Beryllia (Glucina).
Zirconic oxide, ...	Zirconia.

The names of the bases belonging to the second class are formed by changing the terminal syllable of the name of the metal into *ic* or *ous*, and the word hydroxyl into *hydrate.* Thus cæsium and hydroxyl from cæsic hydrate ($Cs(HO)$); barium and hydroxyl, baric hydrate ($Ba(HO)_2$); and iron and hydroxyl, ferric hydrate ($Fe_2(HO)_6$).

A few of these bases have trivial or irregular names, which are almost invariably used instead of the systematic names:

Systematic names.	Irregular names.
Potassic hydrate, ...	Potash.
Sodic hydrate, ...	Soda.
Lithic hydrate, ...	Lithia.

The bases of the third class are distinguished by the terminal syllable *ine*, except nitrine (NH_3), which retains its trivial name ammonia. These bases belong almost exclusively to the department of organic chemistry, and their nomenclature could not be advantageously discussed here.

It has been already mentioned that by the mutual action of an acid and a base upon each other, a *salt* is produced. If the salt be free from oxygen and sulphur, like common salt ($NaCl$), it is termed a *haloid salt;* if it contain oxygen it is termed an *oxysalt;*

and if this oxygen be replaced by sulphur, it is distinguished as a *sulphosalt.*

The haloid salts are named according to the rules of binary compounds above given, thus:

Name.	Formula.
Sodic chloride, . . .	NaCl.
Calcic iodide, ...	$\mathrm{CaI_2}$.
Ferrous bromide, . .	$\mathrm{FeBr_2}$.
Ferric bromide, . . .	$\mathrm{Fe_2Br_6}$.

Oxysalts are divided into *normal, acid,* and *basic.*

A normal salt is one in which the displaceable hydrogen of the acid (see p. 41) *is all exchanged for an equivalent amount of a metal or of a positive compound radical.*

The following examples will serve to illustrate this definition of a normal, or as it is sometimes incorrectly called, a *neutral* salt, the displaceable atoms of hydrogen in the acid, and the metal by which they have been displaced in the salt, being printed in italics:

Acid.		Normal salt.	
Nitric acid, ...	$\mathrm{NO_3}H$, . .	Sodic nitrate, ...	$\mathrm{NO_3}Na$.
		Calcic nitrate, . . .	$\mathrm{(NO_3)_2}Ca''$.
Sulphuric acid, ...	$\mathrm{SO_4}H_2$, . .	Potassic sulphate, . .	$\mathrm{SO_4}K_2$.
		Calcic sulphate, . . .	$\mathrm{SO_4}Ca''$.
Phosphoric acid, ...	$\mathrm{PO_4}H_3$, . .	Potassic phosphate, . .	$\mathrm{PO_4}K_3$.
		Calcic phosphate, . .	$\mathrm{(PO_4)_2}Ca''_3$.
Hypophosphorous acid, . .	$\mathrm{PO_2H_2}H$, .	Sodic hypophosphite, .	$\mathrm{PO_2H_2}Na$.
Phosphorous acid, ...	$\mathrm{PO_3H}H_2$, .	Potassic phosphite, . .	$\mathrm{PO_3H}K_2$.
Metaphosphoric acid, . . .	$\mathrm{PO_3}H$, . .	Lithic metaphosphate, .	$\mathrm{PO_3}Li$.
Pyrophosphoric acid, . . .	$\mathrm{P_2O_7}H_4$, .	Calcic pyrophosphate, .	$\mathrm{P_2O_7}Ca''_2$.
Nordhausen sulphuric acid, .	$\mathrm{S_2O_7}H_2$, .	Sodic pyrosulphate, . .	$\mathrm{S_2O_7}Na_2$.
Unknown acid, ...	$\mathrm{Cr_2O_7}H_2$, .	Potassic dichromate, .	$\mathrm{Cr_2O_7}K_2$.

An acid salt is one in which the displaceable hydrogen of the acid is only partially exchanged for a metal or positive compound radical.

The following examples illustrate the constitution and nomenclature of these salts:

Acid.		Acid salt.	
Sulphuric acid, . .	$\mathrm{SO_4}H_2$,	Hydric sodic sulphate, . . .	$\mathrm{SO_4}HNa$.
Carbonic acid, . .	$\mathrm{CO_3}H_2$?	Hydric potassic carbonate, .	$\mathrm{CO_3}HK$.
Phosphoric acid, .	$\mathrm{PO_4}H_3$,	Hydric disodic phosphate, .	$\mathrm{PO_4}HNa_2$.
		Dihydric sodic phosphate, .	$\mathrm{PO_4}H_2Na$.
		Microcosmic salt, ... (Hydric ammonic sodic phosphate.)	$\mathrm{PO_4}H(NH_4)Na$.

Acid salts are produced almost exclusively from polybasic acids.

When the number of bonds of the metal or compound positive radical contained in a salt exceeds the number of atoms of displaceable hydrogen in the acid, the compound is usually termed a basic salt*—as, for instance:

* For an explanation of this term see Chap. VIII.

Acid.		Basic salt.	
Carbonic acid, . .	CO_3H_2,	Malachite, ...	$CO_5H_2Cu''_2$.
		Blue cupric carbonate, . .	$C_2O_8H_2Cu''_3$.
Sulphuric acid, . .	SO_4H_2,	Tribasic cupric sulphate, .	$SO_8H_4Cu''_3$.
		Turpeth mineral, ...	$SO_6Hg''_3$.

These and most, if not all, other basic salts do not differ essentially in their constitution from the normal and acid salts. This will be seen from the arrangement of their atoms given under the heading of the different metals entering into their composition.

The molecular compounds (*q.v.*) which various substances form with water of crystallization may be conveniently termed *aquates.*

The nomenclature of organic bodies is founded upon the same principles as that of inorganic compounds; but its discussion could not be conveniently introduced here.

CHAPTER IV.

LAWS OF COMBINATION.

As soon as chemists began to realize that the various changes which matter undergoes when two or more substances are extracted from some other substance, or unite to form this substance, are not changes in the ultimate nature of matter itself, but only in its mode of combination, it was natural that they should have recourse to the balance in order to determine the quantities of the different kinds of matter entering into each such combination. The results of these determinations are embodied in the following numerical laws, which form the groundwork of the science.

Law of Constant Proportions.—It has already been mentioned that each chemical substance contains its elements always in the same fixed proportions. Red oxide of mercury consists of 12.5 parts by weight of mercury and 1 of oxygen, this proportion being absolutely unvarying. In like manner hydrochloric acid gas always contains 35.5 parts of chlorine to 1 of hydrogen. And in the same proportions in which the elements of a compound may be separated from each other by analysis, they may by synthesis be made to combine. An excess of any one of the elements over and above the quantity required to unite with the rest, will remain unacted upon. If 40 parts of chlorine be brought into contact with 1 part of hydrogen under the conditions which are necessary for the formation of hydrochloric acid, 4.5 parts of chlorine will remain unchanged, and cannot be made to enter into combination.

The above law is known as the *Law of Constant Proportions.* It was in the course of the experimental development of this law that the great fact first became clear, that matter is indestructible, and, as far as experience goes, uncreatable. When carbon is burnt in a vessel containing oxygen it seems to disappear; but if nothing be allowed to escape, and if the vessel be accurately weighed both before

and after the combustion, the weight will be found not to have changed. The carbon has merely combined with the oxygen to form the invisible gas carbonic anhydride. If a burning piece of the metal sodium be now plunged into the carbonic anhydride thus formed, the sodium will combine with the oxygen of the carbonic anhydride, and the carbon will reappear as a fine black dust. In every series of chemical processes, however complicated, the sum of the weights of the final products will be neither more nor less than that of the initial substances.

Law of Multiple Proportions.—In the course of their quantitative researches, chemists found that in some cases the same two elements combined with each other in two or more *different* proportions, to form totally distinct compounds; but as these proportions were always constant for each such compound, this new fact did not in any way contradict the law just stated. A very simple numerical relation regulates this variation. Mercury, for example, forms two compounds with oxygen—the red oxide, in which the proportion of mercury to oxygen is as 12.5 : 1; and a black oxide, in which the proportion is as 25 : 1. The mercury in the first compound is, therefore, to that of the second as 1 : 2. With nitrogen, oxygen forms no fewer than five different compounds:

	Parts by weight of nitrogen.	Parts by weight of oxygen.
Nitrous oxide, . . .	1	0.571
Nitric oxide, ...	1	1.142
Nitrous anhydride, . .	1	1.714
Nitric peroxide, . . .	1	2.285
Nitric anhydride, . . .	1	2.857

The relative proportions of the oxygen uniting with a constant weight of nitrogen in these five compounds are as 1 : 2 : 3 : 4 : 5. In all cases in which one element unites with another in two or more different proportions these proportions are found to be simple multiples of some common factor. This law is known as the *Law of Multiple Proportions.*

Law of Equivalent Proportions.—The foregoing numerical law was discovered by comparing the different weights of the *same* element which combine with a given weight of some other element. But when the weights of *different* elements which combine with a given weight of various other elements were compared, new and surprising numerical relations became manifest. Thus—

	1 part of chlorine	1 part of bromine	1 part of iodine	1 part of oxygen	1 part of sulphur
	Combines with				
Hydrogen, . . .	0.02817	0.0125	0.00787	0.125	0.0625
Sodium, ...	0.6479	0.2875	0.1811	2.875	1.4375
Potassium, . . .	1.099	0.4875	0.3071	4.875	2.4375
Copper, ...	0.891	0.395	0.249	3.95	1.975
Lead, ...	2.908	1.2906	0.813	12.906	6.453

The numbers in each vertical column bear to each other the same proportion; thus, in all the columns—

	Hydrogen	:	Sodium	:	Potassium	:	Copper	:	Lead.
as . .	1	:	23	:	39	:	31.6	:	103.25

It will be noticed that the numbers for hydrogen, sodium, and potassium are the same as those attached to these elements in the column headed "Atomic weight" in the table of elements, p. 38, whilst those for copper and lead are less by one-half than the numbers in the table. The reason of this will be explained later. (See Chapter XII., Electro-chemical Equivalents.)

On the other hand—

	1 part of hydrogen	1 part of sodium	1 part of potassium	1 part of copper	1 part of lead
	Combines with				
Chlorine, . . .	35.5	1.544	0.91	1.123	0.343
Bromine, . . .	80	3.478	2.05	2.531	0.774
Iodine, ...	127	5.522	3.256	4.019	1.229
Oxygen, . . .	8	0 348	0.205	0.253	0.0774
Sulphur, . . .	16	0.696	0.41	0.506	0.1548

Here again, in all the vertical columns—

	Chlorine	:	Bromine	:	Iodine	:	Oxygen	:	Sulphur.
as . .	35.5	:	80	:	127	:	8	:	16

The numbers which express the proportions of chlorine, bromine, and iodine are those given in the table on p. 38; whilst those of oxygen and sulphur are less by one-half.

This law may be expressed thus: The relative proportions by weight in which the members of any series of elements combine with the same quantity of another element are the same for their combinations with any other element.

35.5 parts by weight of chlorine, 80 parts by weight of bromine, 127 parts by weight of iodine, 8 parts by weight of oxygen, and 16 parts by weight of sulphur are said to be equivalent, as each of these weights serves to satisfy the chemical affinity of 1 part by weight of hydrogen. In like manner 1 part by weight of hydrogen, 23 parts by weight of sodium, 39 parts by weight of potassium, 31.75 parts by weight of copper, and 103.5 parts by weight of lead are equivalent. But the members of the first series are also equivalent to those of the second: thus 23 parts by weight of sodium combine with 35.5 parts by weight of chlorine, 39 parts by weight of potassium with 80 parts by weight of bromine, etc., as may easily be calculated from the last table. Thus every element may have an *equivalent weight* assigned to it, according to which it combines with other elements, the equivalent weight of hydrogen being taken as unity.

CHAPTER V.

THE ATOMIC THEORY.

IN order to account for the remarkable relations just described, chemists have adopted a theory concerning the ultimate constitution of matter which is to be found in the systems of some of the ancient Greek philosophers, but which first received a scientific form at the hands of Dalton. Dalton supposed matter to consist of exceedingly minute particles, incapable of further division—*atoms* (ἄτομος, from α privative, and τέμνω, I cut). These atoms possess different weights in the different kinds of elementary matter, but have always the same weight for the same kind. The juxtaposition of different elementary atoms constitutes chemical combination. Thus if the relative weights of the atoms of potassium and chlorine are as 39 to 35.5, and if the formation of potassic chloride consists in the juxtaposition of one atom of the one element to one of the other, then it is evident that potassic chloride can contain its elements only in the proportion of 39 parts by weight of potassium to 35.5 parts by weight of chlorine. If the relative weights of the atoms of mercury and oxygen are as 200 to 16, and if red oxide of mercury is a combination of one atom of each of its elements, it must contain mercury and oxygen in the proportion of 200 to 16. Again, if the black oxide of mercury is a combination of two atoms of mercury with one of oxygen, the proportion of the former to the latter must be as 400 to 16, or the proportion of mercury in the black oxide is to that in the red as 2 to 1 for equal weights of oxygen.

Thus by the hypothesis of atoms, which possess the same weights for the same elementary kind, but different weights for the different elementary kinds of matter, the three great experimental facts of Constant Proportion, Multiple Proportion, and Equivalent Proportion are referred to one general law.

The atomic theory has, since its adoption by Dalton, undergone many developments, particularly in the sharp distinction of atoms from *molecules* (*molecula*, diminutive of *moles*, a mass). The atoms which enter into chemical combination are supposed to be grouped into molecules—"little masses." These latter are again grouped together to form the masses of matter recognizable by the senses. Thus a solid piece of ice, which contains the atomic weights of hydrogen and oxygen in the proportion of 2 to 1, is not to be regarded as having its atoms thrown together indiscriminately; it is supposed to be made up of a vast number of small independent systems, each containing two atoms of hydrogen and one of oxygen. The atoms within the molecule are held together by chemical attraction: the molecules are kept in their places by cohesion. Neither the atoms within the molecule nor the molecules within the mass, are supposed to be in actual contact. When a body expands by heat the distance

between its molecules is increased, and when it contracts by cooling this distance is diminished. Neither the atoms nor the molecules in a solid body are to be conceived as occupying their positions in a state of rest: various considerations, chiefly of a physical nature, lead to the conclusion that they execute some sort of vibratory motion about their positions of equilibrium. The amplitude of vibration increases with the temperature. If the amplitude of vibration of the molecules becomes too great for stability, the molecules detach themselves from their positions of equilibrium, desert the immediate sphere of attraction of the neighboring molecules, and wander about till they fall under the dominion of other molecules, to be again released by their intensity of vibration. This state of things corresponds to liquidity: cohesion is alternately overcome and restored, and hence is weakened. If, however, the energy of the molecules becomes so great as to carry them beyond the reach of their mutual attraction, they shoot forward in straight lines until they strike against other molecules or against the sides of the containing vessel, in which case they rebound and change their direction, sometimes imparting, sometimes receiving energy. This represents the gaseous condition of matter. Up to this point the atoms which compose the molecule have been considered as keeping together during the wanderings of the molecule itself; but if the temperature be raised still higher, it may happen that the vibration of the atoms within the molecule will carry these also beyond the reach of their mutual attraction, in which case some of them may separate from the parent molecule, forming among themselves simpler molecules more capable of existing at a high temperature. This is the phenomenon of decomposition by heat. It is probable that, at sufficiently high temperatures, only elementary matter can exist, and it is possible that even the molecules of the elements (for, as will be shown later, the atoms of the same element combine with each other to form molecules) break up into their component atoms. (See Iodine.)

The motions of the molecules are manifested in the phenomena of the diffusion of liquids and gases.

In order to give some conception of the aims and scope of the atomic theory in its most recent developments, it may be mentioned that modern chemistry seeks to determine not only the nature and number of the atoms in the molecule, but also their arrangement. That there must be a special arrangement is shown by the fact that two or even more totally distinct compounds may exist having the same number of the same atoms in the molecule. Such compounds are termed *isomeric*. The molecule is to be looked upon as a system composed of various members held together by chemical attraction, just as the members of one of the cosmical systems are held together by gravitation. The molecule of acetic acid, for example, contains two atoms of carbon, four of hydrogen, and two of oxygen. To continue the astronomical illustration, the two atoms of carbon are supposed to be united by mutual attraction like the two suns of a double star. One of these suns possesses three planets in the shape of three atoms of hydrogen; the other has two atoms of oxygen as planets; whilst one

of the oxygen planets has an atom of hydrogen annexed to it as a satellite. Of course *all* the members of such a system must attract each other; but the attraction will be greatest between those which, *cœteris paribus*, are by virtue of their position most subject to each other's influence. When the molecule is divided at any point, the two parts, provided the reaction by which the separation has been effected is not too violent, retain their previous arrangement: thus, by heating potassic acetate with caustic alkali, it is possible to divide the molecule of acetic acid at the junction of the two carbon atoms, in which case the one carbon atom retains its three hydrogen atoms, and the other its two oxygen atoms—one of these with an atom of potassium in the place of the hydrogen of acetic acid. In like manner, by the action of phosphorous chloride, the molecule of acetic acid may be divided so as to split off the atom of oxygen with its hydrogen atom attached. Both parts again remain unchanged as regards their internal arrangement.*

The facts on which these assertions are based could not with advantage be introduced into this chapter. They will be fully treated of in their proper place.

To the unscientific mind there is something peculiarly repellent in the atomic theory and in the physical conceptions which it involves. Our notions of a multitude of minute unconnected particles are derived from the sand-heap—the symbol of instability—and to realize that a solid mass, such as an ingot of steel, consists of minute particles suspended in space without actual contact, is certainly at first sight difficult. But the student of science must dismiss from his mind all crude analogies, and learn above all things to distrust his unaided senses, which in scientific matters are by no means so infallible as they are considered to be in everyday life. In transmitting to the mind the phenomena of the external world, the senses first translate these phenomena into a language of their own, which, however admirably adapted for its purpose, is only a symbolical representation of the phenomena themselves. Sound as heard by the ear has no resemblance to the vibrations of the air; red and violet light as they affect the eye are in no way like longer and shorter waves of ether: yet this is what science tells us concerning these phenomena as they exist outside the sentient subject. And the same holds of the other forces of nature. But the object of science is to perceive the phenomena as they are in themselves—stripped of the interpretation put upon them by the senses. Hence it is that many of the greatest discoveries have apparently contradicted the evidence of the senses.

The magnificent generalization of the conservation of energy, a pendant to that of the indestructibility of matter, has given to the dynamical sciences a unity which they formerly lacked, and has laid down the lines of their future progress. Just as, when we have led an element through a series of combinations with other elements and

* Lucretius (*De Rerum Natura*) has a remarkable passage, which might almost be regarded as an anticipation of the views of modern chemists regarding the constitution of compounds. "It matters much," he says, "with what others and in what position the same atoms are held together."

find that the increase of weight due to the accession of this element has in all cases been the same, and that we can extract the original quantity of the first element, unaltered in all its properties, from its last combination, we conclude that these various compounds, in spite of the difference of their characteristics, all actually contained this given quantity of the same kind of matter; so, when we transform the motion of a mass of matter into the various other forms of energy and find that the quantities are in every case equivalent, and that each of these equivalent quantities can (or could, were it possible to operate without loss) be transformed back into the original quantity of motion of matter, we conclude that all these manifestations of energy actually consisted of the same thing—motion of matter. When the motion of a mass is suddenly arrested, this motion is converted into heat—a motion of the molecules. And in all cases of convertible forms of energy, the amount of this energy, as expressed in terms of the masses and of the velocities, will be the same, whether the masses be sensible masses, or whether they be molecules.

A further refinement of speculation as to the nature of atoms has been introduced by Sir William Thomson in the hypothesis that the ultimate atoms of the elements consist of various forms of vortex rings in a perfect fluid, the ether. This would reduce the different kinds of matter to varieties of motion in one kind of matter, and would account among other things for the indestructibility of matter; it being mathematically demonstrable that a vortex ring in a perfect fluid is indestructible. But it is not necessary in a work like the present to do more than refer to this hypothesis.

Fascinating as all these speculations are, they must never be taken at more than their true value. Even the atomic theory, which explains perhaps as many heterogeneous facts as any other theory, not excepting that of gravitation and the undulatory theory of light—these two theories surpassing it, however, in the important point of their far higher mathematical development—must not be looked upon as more than *the best existing explanation of the facts as at present known*. It may represent the absolute truth; it may be nothing more than a symbolical expression of certain aspects of the truth. The real object of a theory is to group the facts round some central idea from which we may start in our search for fresh facts. The deductions from the theory are the objects of experiment, and by experiment the theory stands or falls. The greater the number of new facts a theory predicts, the better is the theory; but that is all that can be said of it. No number of verified predictions can establish the absolute truth of a theory. Of course this does not refer to those particular cases in which the theory itself may be an ultimately verifiable matter of fact. It can scarcely be so with the atomic theory. No one has ever seen an atom or a molecule, and from theoretical considerations derived from the undulatory theory of light, it is almost certain that no one ever will.

The opposed conception is, that matter fills space continuously and homogeneously. It is impossible to review here the vast array of physical evidence which speaks against this conception and in favor

of the atomic theory: the chemical evidence forms the subject of this work. One chemical fact may, however, be specially mentioned at this point. It has already been stated that the same quantities of the same kinds of matter frequently combine so as to produce two or more totally different compounds. With matter homogeneously filling space this would be inconceivable. Such a difference bespeaks, as was said before, an arrangement of parts. Furthermore, as in the state of the finest mechanical subdivision the particles of a chemical compound all display the same qualities, the parts, by the juxtaposition and arrangement of which the compound is produced, must be exceedingly small. We are thus led back to the atomic theory.

How small the ultimate parts of matter are supposed to be may be judged from Sir William Thomson's calculation that in solids and liquids the mean distance between the centres of contiguous molecules is less than $\frac{1}{140000000}$ and greater than $\frac{1}{4600000000}$ of a centimetre. The molecular vibrations, to which reference has already been made, must of course take place through a correspondingly small range.

CHAPTER VI.

MOLECULAR WEIGHTS.

ALL bodies in the gaseous state are affected equally by pressure. If a given volume of hydrogen and a given volume of chlorine be measured at the pressure of one atmosphere, and if the pressure in each case be then doubled, it will be found that the volume of each has been reduced by one-half. If, on the other hand, the pressure be reduced to half an atmosphere, the original volume of each will be doubled. This relation is expressed by saying that the volume of a gas is, *cæteris paribus*, inversely proportional to the pressure under which it is measured. This law is named from its discoverer *Boyle's Law*. Exceptions to it occur in the case of gases and vapors in the neighborhood of their point of condensation to liquids, when the gaseous condition is imperfect. In these the volume decreases more rapidly than the pressure increases.

In like manner, all bodies in the gaseous state are affected equally by change of temperature. Every gas, when measured at 0° C., expands $\frac{1}{273}$ of its original volume when heated to 1° C., supposing the pressure to remain constant during the operation. This fraction is called the *co-efficient of expansion of gases*. The dilatation takes place in the same ratio for every further increase of temperature: thus if the volume of a gas at 0° be equal to 1, the volume at t° will be $1 + \frac{t}{273.}$ This might also be expressed by saying that, the pressure being constant, the volume of a gas is proportional to its temperature measured from — 273°. Thus the volume of a gas at 20° is to its

volume at 70° as $273 + 20 : 273 + 70$. This law holds for all gases, subject to the deviations mentioned in the case of Boyle's Law. The relation of the volume of gases to temperature was discovered by Charles.

The kinetic theory of gases, a theory at present almost universally accepted by physicists, explains the elasticity and pressure of a gas as the result of the shock of its molecules against the sides of the vessel in which it is contained. If the volume of the gas be reduced by one-half, the number of molecules which strike against the unit of surface in unit of time will be doubled; and hence the pressure will be doubled. If the temperature be raised, the velocity of the molecules, and hence their energy, will be increased: the shock against the sides of the vessel is more intense and also more frequent, hence the pressure will be greater. All gases behave in exactly the same manner in regard to temperature and pressure, and the only satisfactory explanation of this uniformity is the assumption that *equal volumes of all gases at the same temperature and pressure contain an equal number of molecules.* In fact this assumption has been deduced as a law by strict mathematical processes from the kinetic theory of gases.*

This law was first stated as a hypothesis by Avogadro in 1811. It excited little attention at the time, but is now one of the chief foundations of modern chemical theory.

As equal volumes of all gases contain equal numbers of molecules, it is evident that the molecular weights of gaseous bodies will be proportional to the weights of equal volumes at the same temperature and pressure, *i.e.*, to their specific gravities or vapor-densities. If the molecular weight of hydrogen, as the lightest known gas, were to be taken as unity, the molecular weights of other gases would be expressed by the number of times that their specific gravity is greater than that of hydrogen. As will be shown later, however, the molecule of hydrogen consists of two atoms. Since, therefore, its atomic weight is taken to be equal to 1, its molecular weight will be 2. Let the unknown molecular weight of a gas be M, and let its specific gravity (referred to that of air as unity), as found by experiment, be d, then since the specific gravity of hydrogen is 0.0693:

$$0.0693 : 2 = d : M$$

and

$$M = 28.86\, d,$$

or, expressed in words, the molecular weight of a gas may be found by multiplying its specific gravity (referred to that of air as unity) by 28.86. From what has been said above, it is evident that the term gas will here include the vapors of all substances, solid or liquid, capable of volatilizing without decomposition.

If, on the other hand, the specific gravity of the gaseous body is referred to that of hydrogen as unity, then, calling this specific gravity D, we should have

* See Clerk Maxwell, *Theory of Heat*, 3d edition, p. 296.

$$1:2 = D:M$$

or

$$M = 2D.$$

That is to say, the molecular weight of a substance is found by doubling its specific gravity in the gaseous state, the specific gravity of hydrogen being taken as unity.

It is evident that the molecular weight will be equal to the sum of the atomic weights of all the atoms contained in the molecule. (See Atomic Weights.)

Since in nearly every case of chemical action between two or more substances, it is the molecules of these substances which act on each other—either by exchange of atoms or by direct union—and since equal volumes of gas contain, *cæteris paribus*, equal numbers of molecules, it might be expected that in chemical action between gaseous bodies the volumes entering into reaction would present some simple relation to each other. Not only is this the case, but the gaseous volume of the product of the reaction also follows a very simple law. Thus:

1 vol. of hydrogen	+ 1 vol. of	chlorine	yield 2 vols. of	hydrochloric acid.
1 " "	+ 1 "	bromine vapor	" "	hydrobromic acid.
2 vols. "	+ 1 "	sulphur vapor	" "	sulphuretted hydrogen.
2 " "	+ 1 "	oxygen	" "	steam.
3 " "	+ 1 "	nitrogen	" "	ammonia.

The law of combination by volume was discovered by Gay-Lussac.

If the number of molecules in one volume be called n, the first of the above combinations might be written thus: n molecules of hydrogen combine with n molecules of chlorine to form $2n$ molecules of hydrochloric acid. As each of the $2n$ molecules of hydrochloric acid contains both hydrogen and chlorine, each of the n molecules of hydrogen and each of the n molecules of chlorine must have been divided into two parts in order to furnish hydrogen and chlorine for these $2n$ molecules. The molecule of hydrogen therefore consists of *at least* two atoms of hydrogen. The molecule of chlorine is likewise *at least* diatomic. Reasons will be given latter for the belief that the number of atoms in the molecules of these elements is not greater than two.*

The combination by volume may therefore be written: $2n$ atoms of hydrogen combine with $2n$ atoms of chlorine to form $2n$ molecules of hydrochloric acid; or, dividing by $2n$: 1 atom of hydrogen combines with 1 atom of chlorine to form 1 molecule of hydrochloric

* The supposition that the molecules of the great majority of the elements consist of mutually combined elementary atoms, throws light upon a number of otherwise inexplicable phenomena. Thus elements in the so-called *nascent state*—that is, at the moment at which they are released from their combinations—display much more powerful affinities, and are much more capable of effecting chemical changes than when in the *free* state. The explanation is that in the nascent state, it is the single atoms which are released from combination, and that being endowed with free affinities they are especially ready to enter into any fresh combination; whereas in the case of the free element, the atoms have combined with each other to form molecules: not only therefore have the atoms no longer any free affinities, but their mutual combination has to be broken up before they can enter into union with other elements.

acid. That is to say, if we represent in this case the atomic proportion of each of the combining elements by one volume, the molecular proportion of the resulting compound will be represented by two volumes. The same holds of all the combinations given in the above list; thus we may write: 2 atomic proportions (or volumes) of hydrogen combine with 1 atomic proportion (or volume) of oxygen to form 1 molecular proportion (= 2 volumes) of steam.

This is what is meant by the elliptical and somewhat misleading expression frequently employed, that the molecule of a compound occupies in the gaseous state two volumes. In every case, if we take such proportions by volume of the gaseous elements as will represent the atomic proportions* of these elements uniting to form a compound, the molecular proportion of this compound, if measured in the gaseous state, will occupy two volumes. Further, as equal volumes of all gaseous substances contain an equal number of molecules, it is evident that the molecular proportion of these various combining elements will also be represented in the gaseous state by two volumes.

But though the molecular proportion may in every case be represented by two volumes, it by no means follows that the atomic proportion of the gaseous elements may always be represented by one volume, though this happens to be the case in the series of combinations given in the foregoing list. In order to ascertain what volume of a gaseous element corresponds to its atomic proportion when the molecular proportion is represented by two volumes, it is necessary first to ascertain how many atoms the molecule of that element contains. This may be found by dividing the molecular weight, as deduced from the vapor-density, by the atomic weight, as determined by one or more of the methods given in the next chapter.

Name of element.	Molecular weight.	Atomic weight.	Number of atoms in molecule.
Mercury,	200	200	1
Cadmium,	112	112	1
Zinc,	65	65	1
Hydrogen,	2	1	2
Oxygen,	32	16	2
" (as ozone),	48	16	3
Chlorine,	71	35.5	2
Bromine,	160	80	2
Iodine,	254	127	2
Nitrogen,	28	14	2
Sulphur (at 524°),	192	32	6
" (at 860°),	64	32	2
Selenium,	158	79	2
Tellurium,	256	128	2
Phosphorus,	124	31	4
Arsenic,	300	75	4†

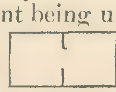
* See following paragraph.

† This list contains all the elements of which the vapor-density has been determined, and, consequently, all the elements of which the molecular weight is known; for though other methods of ascertaining the molecular weight will be described,

The number of atoms contained in the molecules of the various elements is therefore not always the same.* Thus in the case of mercury, cadmium, and zinc, the molecular weight is identical with the atomic weight: the molecules of these elements are *monatomic*. With hydrogen, oxygen, chlorine, nitrogen, and various other elements, the molecular weight is twice as great as the atomic weight: the molecules are *diatomic*. In oxygen in the form of ozone, on the other hand, the molecule is *triatomic*. Phosphorus and arsenic are examples of *tetratomic* molecules, while the molecule of sulphur is *hexatomic* at 524°, and *diatomic* at 860°, the heavy hexatomic molecule breaking up into three lighter diatomic molecules as the temperature rises.

Kundt and Warburg, by a determination of the velocity of sound in mercury vapor, have shown that in the case of this vapor there is no increase of "specific heat at constant volume" due to motion of atoms within the molecule, as is the case with gases having molecules containing more than one atom. The molecule of mercury in the gaseous state must therefore be assumed to be truly monatomic. From this it follows that diatomic molecules really contain only two atoms, triatomic molecules only three atoms, etc.

It is evident that, whatever volume of a gas is adopted to represent its molecular proportion, the volume required to represent its atomic proportion will be inversely as the number of atoms in the molecule of that gas. If, therefore, the molecular proportion is represented by two volumes, the volume corresponding to the atomic proportion will be found by dividing this *molecular volume* by the number of atoms in the molecule. Thus we find that for a monatomic gas, the volume representing one atomic proportion—or, as it may be termed, the *atomic volume*—is two volumes; for a diatomic gas one volume; for a tetratomic gas, half a volume, and so on.

A very convenient expression of these relations is afforded by a notation devised by A. W. Hofmann. In this notation one volume of an element in the gaseous state is represented by a square , within which is written the symbol of the element in question, the atomic volume of this element being unity; two volumes by a double square, open in the middle ; and half a volume by a triangle . Thus in the case of the elements, these symbols would be employed as follows:

only that of vapor-densities is applicable in the case of elements. All other elements are either non-volatile or volatilize at temperatures and under conditions such as to render the determination of their density in the gaseous state a problem beyond the present resources of chemistry. Silver, for example, is volatile only at the temperature of the oxyhydrogen flame. Again, potassium and sodium, though volatile at relatively low temperatures, yield vapors which attack and combine with the material of the vessels employed, and in this way furnish discrepant and untrustworthy results. Hence the molecular weight of all elements other than those contained in the above table is at the present moment purely a matter of surmise.

* From this it follows that the vapor-density alone of an element furnishes no clue to its *atomic* weight.

Name of element.	Atomic volume in the gaseous state.	Molecular volume in the gaseous state.
Mercury, ...	Hg	Hg
Cadmium, ...	Cd	Cd
Zinc, ...	Zn	Zn
Hydrogen, ...	H	H_2 *
Oxygen, ...	O	O_2
Chlorine, ...	Cl	Cl_2
Bromine, ...	Br	Br_2
Iodine, ...	I	I_2
Nitrogen, ...	N	N_2
Sulphur (at 860°), . .	S	S_2
Selenium, ...	Se	Se_2
Tellurium, ...	Te	Te_2
Phosphorus, ...	P	P_4
Arsenic, ...	As	As_4

In the case of compounds, the symbol of the compound (see Chemical Notation) is written within the double square representing the molecular volume in the gaseous state, thus:

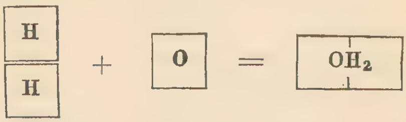
Name of compound.	Molecular volume in the gaseous state.
Hydrochloric acid, ...	HCl
Water, ...	OH_2
Ammonia, etc., ...	NH_3

These volume-symbols may be combined into equations (see Chemical Notation), which will thus express the relative volumes

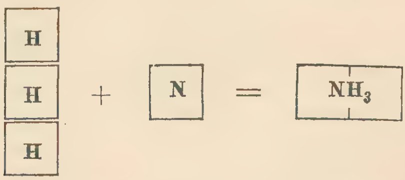
* The small subscript Arabic numeral indicates how many atoms of the element represented by the atomic symbol are present (see Chemical Notation).

of the gaseous elements or compounds taking part in any chemical action, and the volume of the resulting product or products. Thus:

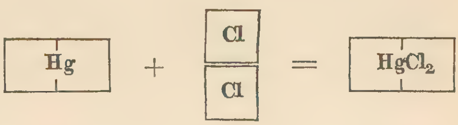
or one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrochloric acid.



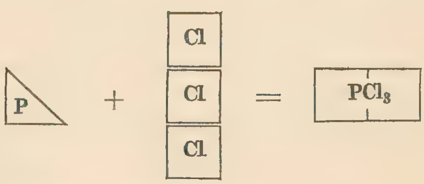
or two volumes of hydrogen combine with one volume of oxygen to form two volumes of steam.



or three volumes of hydrogen combine with one volume of nitrogen to form two volumes of ammonia.



or two volumes of mercury vapor combine with two volumes of chlorine to form two volumes of the vapor of mercuric chloride.



or half a volume of phosphorus vapor combines with three volumes of chlorine to form two volumes of the vapor of phosphorus chloride.

Of course in reality these chemical reactions take place not between atoms, but between molecules, and the reaction of hydrogen with chlorine, for example, would therefore have to be written:

but the above simplified mode of expression has been adopted in order that the molecule of the resulting compound may in every case be represented by two volumes.

To the definitions of the terms molecule and atom already given, the following may be added:

The molecule of an element or of a compound is the smallest portion capable of existing in a free state—at all events during any appreciable interval of time. An atom of an element is the smallest part of that element capable of entering into or being expelled from a chemical compound—the smallest part that exists in the molecule of any of its compounds. The atomic weight of an element expresses the number of times its atom is heavier than the atom of hydrogen. The molecular weight of an element or compound is, as already stated, the sum of the atomic weights of the atoms in its molecule.

The various methods of determining vapor-densities will be fully described in the part of this work relating to organic chemistry: they are of great importance in fixing the molecular weights of organic compounds. The principles involved in these methods may be stated in a few words. The method of Dumas, applicable both to gases and to vapors, consists in ascertaining the weight of that quantity of the substance which in the gaseous state occupies a known volume. In the method of Gay-Lussac, which can be employed only in the case of vapors, the reverse principle—that of ascertaining the volume occupied in the gaseous state by a known weight of substance—is employed. In both cases the temperature of the gas or vapor, and the pressure at which it is measured, must be carefully noted. The relation of the weight of a given volume of substance in the gaseous state to the weight of an equal volume of air or hydrogen at the same temperature and pressure, constitutes the vapor-density of the substance. In order that results obtained in the measurement of gases and vapors may be comparable, it is usual to calculate what the volumes would have been had the measurement been made under the pressure of 760 millimetres of mercury (this being the average pressure of the atmosphere), and at the temperature of 0° C. This process is known as "reduction to standard temperature and pressure." It is employed even in cases where the substance does not exist in the gaseous state under these conditions of temperature and pressure. Any other temperature and pressure might have been chosen, and the relations of the volumes of different gases so reduced would have remained exactly the same. If v be the volume of a gas or vapor measured at the temperature of $t°$ C., and under the pressure of p millimetres of mercury, its volume V at 0° C and 760 millimetres will be:

$$V = \frac{vp}{760(1 + \frac{t}{273})}.$$

This formula may easily be deduced from the laws of Boyle and Charles.

All other direct methods of determining vapor-densities are modifications of the two just mentioned.

The method of ascertaining the molecular weight from the vapor-density is unfortunately limited in its application. Allusion has already been made (p. 56) to the practical impossibility of determining the vapor-density in the case of the great majority of the elements. As regards compounds, many of these decompose in assuming the gaseous state, so that their vapors consist of molecular mixtures more or less heterogeneous, from the density of which no conclusion can be drawn as to the molecular weight of the original compound.

In the case of such compounds, an indirect method has to be resorted to. It will be best to illustrate the application of this method by a case in which the molecular weight has already been deduced from the vapor-density.

The analysis of a compound gives a certain percentage composition, from which an empirical formula may be calculated. In this way the empirical formula CH_2O is obtained for acetic acid. But it is evident that any multiple of this formula, $C_2H_4O_2$, $C_3H_6O_3$, etc., would correspond equally well with the same percentage composition, and the question therefore arises, which is the true molecular weight? Experiment shows that 107.7 parts by weight, or 1 atom of silver, may be substituted for 1 part of hydrogen in acetic acid; and further, that in this manner one-fourth part of the entire hydrogen present in the acid may be displaced. As fractions of atoms do not exist, the only legitimate conclusion is that the number of atoms of hydrogen in the molecule of acetic acid is four, or some integer multiple of four. At this point the decision is rendered easy by the knowledge derived from other sources that acetic acid belongs to the class of the monobasic acids in the molecule of which only one atom of hydrogen can be displaced by silver. Hence the molecular formula of acetic acid must be $C_2H_4O_2$. Adding together the atomic weights (see table, p. 38) of all the atoms in the molecule, the molecular weight 60 is obtained.

Now the vapor-density of acetic acid determined at 300° has been found to be 2.08 (air = 1). Substituting this value for d in the formula $M = 28.9 \times d$, we find $M = 60.1$ as the molecular weight of acetic acid, a number which agrees very well, within the limits of experimental error, with that deduced above.

As the operations of weighing, on which the determinations of the atomic weights depend, can be performed with greater accuracy than those involved in ascertaining vapor-densities, it is usual to select as the most trustworthy the molecular weight obtained by adding together the atomic weights of all the atoms in the molecule, using the vapor-density only to decide between two or more possible molecular weights. Thus in the case of acetic acid, the formulæ CH_2O, $C_2H_4O_2$, and $C_3H_6O_3$ would represent the molecular weights 30, 60, and 90 respectively. The number 60.1 obtained from the vapor-density leaves no doubt as to which of these is the true molecular weight.

Melissic acid is a compound of high molecular weight, not volatile

without decomposition. Its whole chemical behavior shows that it belongs to the same class of acids as acetic acid; this knowledge is of use in determining the molecular weight. The empirical formula is $C_{15}H_{30}O$, which would correspond to the molecular weight 226. We have already seen that 107.7 parts of silver can displace 1 part of hydrogen in 60 parts of acetic acid. In like manner experiment shows that 1 part of hydrogen in 452 parts of melissic acid may be displaced by 107.7 parts of silver. The molecular formula of this acid is therefore $C_{30}H_{60}O_2 = 452$, or twice as great as the empirical formula, as was also the case with acetic acid.

When a substance is not volatile without decomposition, and is moreover incapable of forming compounds from which conclusions can be drawn as to its molecular weight, the determination of this latter is beset with still greater difficulties. In this case it is necessary to take the compound, as it were, to pieces, either by breaking it up into two or more known compounds, or by destroying one part and leaving the rest intact, the object being in every case to arrive at compounds of known molecular weight. In this way more or less trustworthy conclusions as to the molecular weight of the original compound may sometimes be arrived at; but this method is far inferior in the certainty of its results to the two already described.

CHAPTER VII.

ATOMIC WEIGHTS.

1. Deduction of the Atomic Weight of an Element from the Vapor-density of its Compounds.

The atomic weight of an element is that weight which is the greatest common divisor of the various weights of that element occurring in the molecules of its compounds, the atomic weight of hydrogen being taken as unity. The atomic weights are thus relative, not absolute weights.

As the molecular weights of volatile elements and of those compounds which can be vaporized without decomposition have alone been determined with certainty (all other methods, whatever probability of accuracy their results may possess, being based more or less on analogy), it is necessary, in order to determine the atomic weight of an element according to the above definition, that it should form a number of compounds volatile without decomposition. The following tables show the application of this method:

1 mol.	Mol. weight.	Contains parts by weight.	Mol. formula.
Hydrogen, ...	2	2 Hydrogen, ...	H_2.
Chlorine, ...	71	71 Chlorine, ...	Cl_2.
Oxygen, ...	32	32 Oxygen, ...	O_2.
Sulphur, ...	64	64 Sulphur, ...	S_2.
	192	192 Sulphur, ...	S_6.
Nitrogen, ...	28	28 Nitrogen, ...	N_2.
Hydrochloric acid, . .	36.5	1 Hydrogen, 35.5 chlorine, . . .	HCl.
Hydrocyanic acid, . .	27	1 Hydrogen, 12 carbon, 14 nitrogen,	HCN.
Nitric oxide, ...	30	14 Nitrogen, 16 oxygen, ...	NO.
Nitrous oxide, . . .	44	28 Nitrogen, 16 oxygen, ...	N_2O.
Water, ...	18	16 Oxygen, 2 hydrogen, ...	OH_2.
Carbonic oxide, . . .	28	12 Carbon, 16 oxygen, ...	CO.
Carbonic anhydride, .	44	12 Carbon, 32 oxygen, ...	CO_2.
Methylic hydride, . .	16	12 Carbon, 4 hydrogen, ...	CH_4.
Methylic chloride, . .	50.5	12 Carbon, 3 hydrogen, 35.5 chlorine,	CH_3Cl.
Methylenic dichloride,	85	12 Carbon, 2 hydrogen, 71 chlorine,	CH_2Cl_2.
Chloroform, ...	119.5	12 Carbon, 1 hydrogen, 106.5 chlorine,	$CHCl_3$.
Carbonic tetrachloride,	154	12 Carbon, 142 chlorine, ...	CCl_4.
Dicarbonic hexachloride,	237	24 Carbon, 213 chlorine, ...	C_2Cl_6.
Acetone, ...	58	36 Carbon, 6 hydrogen, 16 oxygen,	C_3H_6O.
Methylic oxalate, . .	118	48 Carbon, 6 hydrogen, 64 oxygen,	$C_4H_6O_4$.
Sulphuretted hydrogen,	34	32 Sulphur, 2 hydrogen, ...	SH_2.
Disulphur dichloride, .	135	64 Sulphur, 71 chlorine, ...	S_2Cl_2.
Sulphurous anhydride,	64	32 Sulphur, 32 oxygen, ...	SO_2.
Boric fluoride, . . .	68	11 Boron, 57 fluorine, ...	BF_3.
Silicic fluoride, . . .	104.2	28.2 Silicon, 76 fluorine, ...	SiF_4.

In the next table the above results are arranged so that the atomic weights of the various elements under discussion may be deduced. The first column contains the name of the element; the second, the relative weights of it occurring in the molecules of its compounds above enumerated—the smallest of these weights, which *generally* coincides with the atomic weight, being placed first; and the third, the greatest common divisor of these numbers, this last being identical with the atomic weight:

Element.	Relative weights.	G. C. D.
Hydrogen, ...	1, 2, 3, 4, 6, ...	1
Chlorine, ...	35.5, 71, 106.5, 142, 213, ...	35.5
Oxygen, ...	16, 32, 64, ...	16
Sulphur, ...	32, 64, 192, ...	32
Nitrogen, ...	14, 28, ...	14
Carbon, ...	12, 24, 36, 48, ...	12
Fluorine, ...	57, 76, ...	19

In this way the atomic weights of these elements have been determined.

It will be noticed that the smallest relative weight of fluorine occurring in the molecule of either of its compounds above mentioned is thrice its atomic weight. A compound, hydrofluoric acid, con-

taining one atom of fluorine to one of hydrogen, has long been known, but, though capable of existing as a gas even at ordinary temperatures, its vapor-density could not be ascertained, owing to its property of attacking the vessels of glass or porcelain in which it has to be measured. Latterly, however, the problem has been solved, and hydrofluoric acid is found to possess the molecular formula $HF = 20$,* and to consist of 19 parts of fluorine to 1 of hydrogen. Organic compounds of fluorine, containing only one atom of this element in the molecule, have also been discovered. They are volatile and do not attack glass, so that their vapor-density may be determined in the ordinary way. The existence of these compounds places the number now accepted as the atomic weight of fluorine on a much surer basis.

It is evident that the above method alone can never afford absolute certainty as to the atomic weights of the elements, since we can never be sure that a compound will not be discovered containing in its molecule either a smaller relative weight of an element than that which has been deduced from the known compounds of that element, or some relative weight which is not a rational multiple of the received atomic weight. If, for example, a compound containing 8 parts, or 24 (or any odd multiple of 8) parts of oxygen in the molecule were to be discovered, it would be necessary to change the atomic weight of oxygen from 16 to 8. Fortunately, however, two other methods of fixing the atomic weight are known (see pp. 65 and 67), and the agreement prevailing between the numbers determined by these three totally independent methods, increases enormously the probability of their correctness.

Apparent Exceptions to Avogadro's Law.—There are cases in which the molecular weights as deduced from the vapor-densities give values which are less than the sum of the weights of the smallest possible number of whole atoms which can go to form the compound. The following three substances, at ordinary temperatures solids, will serve as illustrations:

The vapor-density of ammonic chloride has been found to be 0.89 (air = 1). The molecular weight would therefore be

$$M = 28.9 \times 0.89 = 25.7.$$

The smallest stœchiometric† molecule is

$$NH_4Cl = 53.5 = 2 \times 26.75.$$

The molecular weight deduced from the vapor-density would therefore correspond to the formula $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$: in other words, the accepted atomic weights of nitrogen and chlorine would have to be halved.

Phosphoric chloride has a vapor-density of 3.65, or only half of that required by its smallest stœchiometric formula PCl_5. The formula

* The above is the molecular weight of hydrofluoric acid at 100°. At 25° it has the molecular weight 40, corresponding to the molecular formula H_2F_2. This in no way invalidates the foregoing conclusions.

† *Stœchiometric*, pertaining to the atomic weights.

would therefore have to be written $P_{\frac{1}{2}}Cl_{\frac{5}{2}}$, and the atomic weights of phosphorus and chlorine would have to be halved.

A still worse complication is introduced by the vapor-density of ammonic carbamate, which is 0.89, or only one-third of that which its smallest possible formula $N_2H_6CO_2$ demands. The molecular formula would therefore be $N_{\frac{2}{3}}H_2C_{\frac{1}{3}}O_{\frac{2}{3}}$.

In order to introduce whole numbers of atoms into this last formula, and at the same time into that of ammonic chloride, $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$, it would be necessary to give to the atomic weight of nitrogen a value only one-sixth of that now assigned to it, or 2.33 instead of 14. This would further involve the assumption that nearly all the other compounds of nitrogen contain at least six atoms of nitrogen.

Fortunately, however, these alterations, which would introduce indescribable confusion into chemistry, would also be erroneous. It has been proved that all these compounds decompose in volatilizing. The molecule of ammonic chloride (NH_4Cl) breaks up into one molecule of ammonia (NH_3) and one of hydrochloric acid (HCl). The vapor thus contains twice as many molecules as it would have done had no decomposition taken place; it therefore occupies twice the volume, and consequently possesses only half the density. The same holds good concerning phosphoric chloride (PCl_5), which breaks up into equal molecules of phosphorous chloride (PCl_3) and free chlorine (Cl_2). Ammonic carbamate ($N_2H_6CO_2$) decomposes into two molecules of ammonia (NH_3, NH_3) and one of carbonic anhydride (CO_2), so that the volume is three times, and the density only one-third as great as would be the case if no decomposition had taken place. Since in all these cases the products of decomposition recombine on cooling to form the original compound, the difficulty lay in proving that a decomposition had really taken place. However, this has been satisfactorily accomplished by various methods, both direct and indirect; so that it is not necessary either to doubt the validity of Avogadro's law, as some chemists were inclined to do, or to introduce intricate and contradictory changes in the accepted atomic weights.

2. Determination of the Atomic Weights by means of Isomorphism.*

Many different compounds crystallize in the same or nearly the same forms. For example, the salts

Plumbic nitrate, ...	PbN_2O_6.
Baric nitrate, ...	BaN_2O_6.
Strontic nitrate, ...	SrN_2O_6.

crystallize in the same forms of the regular system (see Crystallography). As any given form of the regular system has invariably the same angles, the identity of form in the above three cases is absolute. Again:

* The selection of examples of isomorphism is borrowed from Kopp's *Theoretische Chemie.*

Nickelous sulphate, ...	$NiSO_4,6OH_2$,
Nickelous seleniate, ...	$NiSeO_4,6OH_2$,
Zincic seleniate, ...	$ZnSeO_4,6OH_2$,

crystallize in the same quadratic forms, with angles almost identical in the three cases, and with the same cleavage.* The following compounds:

Zincic sulphate, ...	$ZnSO_4,7OH_2$,
Nickelous sulphate, ...	$NiSO_4,7OH_2$,
Magnesic sulphate, ...	$MgSO_4,7OH_2$,
Magnesic seleniate, ...	$MgSeO_4,7OH_2$,
Magnesic chromate, ...	$MgCrO_4,7OH_2$,

crystallize in very similar forms of the rhombic system, with almost the same angles.

Compounds which, like the above, crystallize in the same or nearly the same forms, and possess similar constitution, are termed *isomorphous.* In an isomorphous group those elements which occur in all the members are called the *common elements;* those which may be varied without producing a change of crystalline form, the *corresponding elements.* The corresponding elements are frequently termed the *isomorphous elements,* although they do not, when isolated, *necessarily* crystallize in the same forms. The sense in which the term *isomorphous* is used when applied to compounds must not be confounded with that which it bears in reference to elements. In the former case it means: "possessing the same form;" in the latter, "producing the same form."

In each of the above groups it will be noticed that all the compounds contain the same number of atoms. It has further been found by experiment that in an isomorphous group, the corresponding elements occur in the relative proportions of their atomic weights as determined by Avogadro's law. Hence it is only necessary to know the atomic weight of one of the corresponding elements in a group of isomorphous compounds in order to determine the atomic weights of all the rest. But before illustrating this, it will be necessary to describe the various groups of *isomorphous elements.* In such a group the analogous compounds which the various members form with the same element or elements are frequently, but not necessarily, isomorphous.

1. *Sulphur, Selenium, Manganese, Chromium.*—Sulphides and selenides are frequently isomorphous, for instance: PbS and PbSe, Ag_2S and Ag_2Se. The salts of sulphuric, selenic, manganic, and chromic acids, with the same base, and containing the same number of molecules of water of crystallization, are generally isomorphous.

2. *Magnesium, Calcium, Manganese, Iron, Cobalt, Nickel, Zinc, Cadmium, Copper.*—The carbonates of these metals crystallize in rhombohedra with rhombohedral cleavage. The cleavage rhombohedra have almost the same angles. The sulphates are also for the most part iso-

* *Cleavage* is the tendency which some crystallized substances display when broken, to split in directions parallel to the faces of certain crystalline forms of these substances. The artificial forms thus produced are known as "cleavage forms."

morphous, and the same is the case with the double sulphates of these metals with potassium and ammonium.

3. *Manganese* and *Iron*, both members of the preceding group, also form another group with *Chromium* and *Aluminium*. The three sesquioxides Fe_2O_3, Cr_2O_3, and Al_2O_3, are isomorphous. The sesquioxides of these four metals combine with monoxides of the general formula $R''O$ to form the spinelles, which all crystallize in the regular system and possess the general formula $R''O, R'''_2O_3$. The sesquioxides also enter into the composition of the alums, which all crystallize in the regular system.

4. *Calcium* has also isomorphous relations with *Strontium*, *Barium*, and *Lead*. All four are connected by their carbonates (calcium as arragonite); calcium and lead by their tungstates; strontium, barium, and lead by their anhydrous sulphates.

A simple enumeration of some of the remaining isomorphous groups must suffice:

5. *Tungsten* and *Molybdenum*.
6. *Tin* and *Titanium*.
7. *Palladium, Platinum, Iridium*, and *Osmium*.
8. *Potassium* and *Ammonium*.
9. *Sodium* and *Silver*.
10. *Phosphorus, Arsenic*, and *Antimony*.
11. *Chlorine, Bromine, Iodine*.

Elements which are isomorphous with the same element are not necessarily isomorphous with each other. It would be incorrect, for example, to say that iron and sulphur must be isomorphous because they are both (in different ways) isomorphous with manganese. Only those elements can be said to be isomorphous which occur in the same true group of isomorphous compounds; and in a true group of isomorphous compounds all the members possess *the same crystalline form and an analogous atomic composition.*

It only remains to give an illustration of the method of applying the law of isomorphism to the determination of the atomic weights. From the vapor-density of their compounds, chlorine and sulphur have been found to possess the atomic weights $Cl = 35.5$ and $S = 32$. In the isomorphous sulphates and manganates (isomorphous group 1), the corresponding elements occur in the proportion of 32 parts by weight of sulphur to 55 of manganese. In the isomorphous perchlorates and permanganates, the proportion in which the corresponding elements occur is 35.5 parts of chlorine to 55 of manganese. The atomic weight of manganese is therefore 55. But the metals of the 2d isomorphous group are contained in their isomorphous carbonates and sulphates in the following relative proportions: manganese 55, magnesium 24.4, calcium 40, iron 56, cobalt 58.6, nickel 58.6, zinc 65.3, cadmium 112, copper 63.2; and these are therefore the atomic weights of those elements. In like manner it is only necessary to refer the proportions in which the metals of the 4th isomorphous group occur in their isomorphous compounds to the atomic weight of calcium just deduced, $Ca = 40$, in order to determine the atomic weights of barium, strontium, and lead, which are thus found to be $Ba = 137$, $Sr = 87.5$, $Pb = 206.5$.

The foregoing enumeration of isomorphous groups includes only some of the most prominent. There are many others which serve as connecting links, so that it is possible by means of the law of isomorphism to determine the atomic weights of nearly all the elements.

Isomorphous compounds possess the property of crystallizing together in various proportions to form homogeneous crystals belonging to the same system as the compounds themselves. These crystals are generally distinguished by possessing simpler forms—less variety of faces—than the crystals of the pure compounds. If the angles of the latter differ slightly from each other, the angles of the mixed crystals will possess values which lie between those of the pure compounds. Thus the terminal angle of the cleavage rhombohedron of pure calcium carbonate is 105° 5′; that of pure magnesic carbonate, 107° 25′; whilst in the case of their isomorphous mixtures, this angle varies between these two limits, inclining in the direction of the compound which predominates in the mixture.

A substance which crystallizes in two different forms not reducible to the same system is termed *dimorphous*. It sometimes happens that two dimorphous compounds are isomorphous, in which case the two distinct forms frequently correspond in the two compounds. This double isomorphism is known as *isodimorphism*. Antimonious oxide, Sb_2O_3, occurs naturally in regular octahedra as senarmontite, and in rhombic prisms as valentinite. Arsenious anhydride, As_2O_3, is found in nature in regular octahedra as arsenic bloom and in rhombic prisms as claudetite, these two forms respectively corresponding with those of antimonious oxide, with which arsenious anhydride is thus isodimorphous.

The law of isomorphism was first enunciated by Mitscherlich, in 1819.

The determinations of atomic weights by means of this law are not always absolutely certain. This uncertainty has its root in the fact that various undoubtedly isomorphous compounds are known in which the number of atoms in the molecule is different. Thus the salts of potassium (K) and ammonium (NH_4) are isomorphous. Baric permanganate, $BaMn_2O_8$, is isomorphous with anhydrous sodic sulphate, Na_2SO_4. In none of these compounds can the corresponding *elements* be said to be substituted for each other in the proportion of their atomic weights.

3. Determination of the Atomic Weights from the Specific Heats of the Elements in the Solid State.

If a kilogram of water at 100° be mixed with a kilogram of water at 0°, the temperature of the mixture will be 50°, the mean of the other two temperatures. If a kilogram of iron filings at 100° be mixed with a kilogram of water at 0°, the temperature of the whole will not be higher than 10°. As, therefore, a given weight of water in cooling through 50° can raise the temperature of an equal weight of water through 50°, and as a given weight of iron filings in cooling through 90° can raise an equal weight of water through only 10°, it is evident that equal weights of iron and water at the same *temperature* contain

very different amounts of *heat.* Calculated from the above figures, the quantities of heat contained in equal weights of water and iron at the same temperature will be as $\frac{50}{50}$ to $\frac{10}{90}$, or as 1 to $\frac{1}{9}$. And as the heat which a body gives off in cooling is equal to that which it has taken up in heating, it will require 9 times as much heat to raise the temperature of a given weight of water through a given number of degrees, as it will to raise the same weight of iron through an equal number of degrees. The relative capacities of bodies for heat are known as their *specific heats,* that of water being taken as unity.

For many reasons it is useful to have a *unit of heat,* by means of which the heat evolved or absorbed in chemical or other processes may be measured. For this purpose *that quantity of heat required to raise the temperature of* 1 *gram of water from* 0° *to* 1° *C.* is employed as the standard of measurement, and is known as the *unit of heat, thermal unit,* or *calorie.* As the specific heat of water is the unit of the specific heats, it is evident that in order to find how many units of heat are required to raise the temperature of a body through any number of degrees of the centigrade scale, it will only be necessary to multiply together the weight of the body expressed in grams, its specific heat, and the number of degrees through which its temperature has been raised.* Thus the quantity of heat required to raise the temperature of 2 grams of iron through 90°, or of 180 grams through 1°, or of 1 gram of water through 20°, or of 2 grams through 10°, is in every case the same, namely 20 thermal units.

Dulong and Petit were the first to determine the specific heats of a number of the chemical elements, and they arrived at the remarkable result, that *the specific heats of the elements in the solid condition are inversely as their atomic weights.* If instead of determining the specific heat of equal weights of the elements, the latter be taken in the proportion of their atomic weights, the specific heats of these atomic weights will be equal, or as this may be expressed: *the capacities for heat of the atoms of different elements in the solid state are equal: all the elements in the solid state have the same atomic heat.* The atomic heat may be found by multiplying the specific heat of an element by its atomic weight. The average value of the atomic heat for the different elements is 6.4. The slight variations which the atomic heats of the various elements display, arise first from the difficulty of determining accurately the specific heat, and secondly from difference of physical condition in the elements—the chief disturbing influence depending upon the fact that the specific heat of an element rises with the temperature, being greatest near the fusing point, whilst the specific heats are generally determined between 0° and 100°, and consequently at varying distances from the fusing points of the different elements.

It is evident that the law of Dulong and Petit must offer a very valuable means of checking doubtful atomic weights, and of determining such as are not within the reach of the other two methods. Thus,

* This mode of calculation is based on the assumption that the specific heat of a body is the same at all temperatures, which is only approximately correct. As will be shown later, the specific heat increases with the temperature.

gold forms no volatile compounds, and its isomorphism with other elements is not sufficiently marked to be available as a means of fixing its atomic weight. But the specific heat of gold has been found to be 0.0324, and this number multiplied by 196, the accepted atomic weight of gold, gives 6.35, closely approximating to the average atomic heat of the elements, from which it may be concluded that 196, and no multiple or sub-multiple of this number, is the true atomic weight of gold.

A glance at the table of specific heats on p. 73, in which the elements are arranged in the order of their atomic weights, will show that the deviations from the law of Dulong and Petit follow a certain rule. In the case of the elements of high atomic weight, the agreement is almost always good, and with these elements it is to be noted that the variation of the specific heat with the temperature at which it is determined is but small. The notable exceptions to the law are to be found among the elements which combine the two properties of *low atomic weight and low atomic volume* (*q. v.*). In the following list of these exceptional elements, the specific heats have been determined at temperatures below 100° C. (212° F.). The brackets denote indirect determinations (see Neumann's Law, p. 70):

Name of element.	Atomic heat.
Aluminium,	5.7
Phosphorus,	5.3
Sulphur,	5.1
Nitrogen,	(5)
Fluorine,	(5)
Oxygen,	(4)
Silicon,	3.8
Beryllium (Glucinum),	3.7
Boron,	2.7
Hydrogen,	(2.3)
Carbon (as diamond and in its compounds),	1.8

A reference to Lothar Meyer's curve of the elements (see diagram, Classification of the Elements according to their Atomic Weights) will show that the whole of these exceptional elements are to be found in the lower portions of the first three periods of the curve—a position which, from the nature of this curve, falls to these elements in virtue of their low atomic weight and low atomic volume. That low atomic weight alone is not sufficient to produce deviation from the law of Dulong and Petit, is very clearly shown by the fact that three elements of low atomic weight—lithium, sodium, and potassium—which, however, owing to their relatively high atomic volume, form maxima of the curve, perfectly conform to the law. A straight dotted line, cutting the curve, has therefore been drawn to indicate the "limit of validity of the law of Dulong and Petit." The exceptional elements are all to be found below this line.

It is probable, however, that even for these exceptional elements there is a temperature at which they conform to this law. H. F. Weber, who has carefully determined the specific heats of carbon and silicon for a great range of temperature, finds that the specific heat rapidly

increases with the temperature until a point is reached at which these elements approximately obey the law; that is to say, the deviations are not much greater than in the case of aluminium, thus leaving no reasonable doubt about the atomic weight. Above this point the specific heat rises only very slowly with the temperature. This lower limit of conformity to the law lies in the case of silicon at about 200° C., in the case of carbon about 600° C. It is worthy of note that the various modifications of carbon, which at ordinary temperatures possess widely different specific heats, have the same specific heat as soon as the above limit is reached. Boron shows a similar rapid rise of specific heat; but the observations have not been carried to temperatures sufficiently high to determine the lower limit of conformity in the case of this element; it, however, probably lies between 500° and 600° C.

Dulong and Petit tried without success to extend the law of specific heat to compounds. This was finally accomplished by Neumann (1831), who showed that chemically equivalent quantities of similar compounds have the same capacities for heat. If the product of the molecular weight into the specific heat be termed the *molecular heat* of a compound, this law may be expressed: *Similar compounds have the same molecular heats* For example:

Compound.	Mol. formula.	Mol. weight.	Sp. heat.	Mol. heat.
Lithic chloride, . .	$LiCl$	42.5	0.2821	12
Sodic chloride, . .	$NaCl$	58.5	0.2140	12.5
Potassic chloride, .	KCl	74.5	0.1730	12.9
Argentic chloride, .	$AgCl$	143.2	0.0911	13

It is possible in this way to determine the atomic heat of elements which do not exist at ordinary temperatures in the solid state. Thus, by subtracting from the molecular heat of potassic chloride, 12.9, the atomic heat of potassium, 6.6, the atomic heat of chlorine is found to be 6.3. A study of the above-mentioned chlorides shows that the atomic heat of chlorine thus deduced varies according to the chloride employed; but the method of calculating its value by subtracting the atomic heat of the other element exaggerates these errors. It is further evident that the danger of error in this indirect method of determining the specific heat of an element will be greater the greater the relative number of atoms of other elements contained in the molecule of the compound employed. But if the molecular heat of a compound be divided by the number of atoms in the molecule, the variations caused by difference of physical conditions in different compounds will be distributed among the atomic heats of the several atoms in the molecule (which are probably all affected in the same direction by such variations), and the average atomic heat of the elements contained in that compound will be obtained. Thus the molecular heats of the above chlorides divided by 2 give numbers varying from 6 to 6.5, sufficiently approximating to 6.4, the average atomic heat of the elements in the solid state.

In this way Neumann's law has been successfully applied in verifying the atomic weights of elements, the specific heats of which had not been directly determined. Thus in the case of barium, strontium, and calcium, chemists were in doubt whether these elements possessed the atomic weights Ba = 137, Sr = 87.5, and Ca = 40; or, only the half of these weights, ba = 68.5, sr = 43.8, and ca = 20—these smaller values being formerly universally employed. In these two cases the formulæ of the chlorides would be respectively:

Formula.	Mol. weight.	Formula.	Mol. weight.
$BaCl_2$, ...	208	baCl, ...	104
$SrCl_2$, ...	158.5	srCl, ...	79.3
$CaCl_2$, ...	111	caCl, ...	55.5

The number of atoms in the molecule is in the first case 3, in the second 2. The specific heats of these compounds were found to be:

Baric chloride, ...	0.0902
Strontic chloride, ...	0.1199
Calcic chloride, ...	0.1642

Now the expression $\frac{\text{molecular weight} \times \text{specific heat}}{\text{number of atoms in molecule}}$ ought to be approximately equal to 6.4, the average atomic heat. Substituting in this expression the above values, we find for

$$\text{baCl}, \quad \frac{104 \times 0.0902}{2} = 4.7,$$

$$\text{srCl}, \quad \frac{79.3 \times 0.1199}{2} = 4.75,$$

$$\text{caCl}, \quad \frac{55.5 \times 0.1642}{2} = 4.55;$$

and for

$$BaCl_2, \quad \frac{208 \times 0.0902}{3} = 6.23,$$

$$SrCl_2, \quad \frac{158.5 \times 0.1199}{3} = 6.33,$$

$$CaCl_2, \quad \frac{111 \times 0.1642}{3} = 6.07.$$

The values 6.23, 6.33, and 6.07 approximate with sufficient closeness to 6.4; whereas, 4.7, 4.75, and 4.55 differ widely from this number. The formulæ of the chlorides must, therefore, be written $BaCl_2$, $SrCl_2$, and $CaCl_2$, and the three elements must possess the atomic weights Ba = 137, Sr = 87.5, and Ca = 40. Only a few years ago the specific heat of metallic calcium was determined for the first time by Bunsen, and was found to be 0.1704. This number, multiplied by 40, the

atomic weight of calcium, gives 6.82 as the atomic heat of this element, thus directly proving the correctness of the above deduction.

In applying Neumann's law to compounds in which any of the exceptional elements occur, it is necessary to introduce the special value for the atomic heat in calculating the molecular heat of the compound. In the case of the other elements, the average atomic heat, 6.4, may be employed without sensible error:

Name of compound.	Molecular formula.	Molecular heat.	
		Calculated.	Found.
Antimonious sulphide,	Sb_2S_3.	$(2 \times 6.4) + (3 \times 5.1) = 28.1$	28.6
Potassic pyrophosphate, ...	$K_4P_2O_7$.	$(4 \times 6.4) + (2 \times 5.3) + (7 \times 4) = 64.2$	63.1
Calcic fluoride, . .	CaF_2.	$6.4 + (2 \times 5) = 16.4$	16.3
Cupric oxide, . . .	CuO.	$6.4 + 4 = 10.4$	10.2
Silicic anhydride, .	SiO_2.	$3.8 + (2 \times 4) = 11.8$	11.5
Boric anhydride, . .	B_2O_3.	$(2 \times 2.7) + (3 \times 4) = 17.4$	16.6
Sodic metaborate, . .	$NaBO_2$.	$6.4 + 2.7 + (2 \times 4) = 17.1$	16.9
Dicarbonic hexachloride, ...	C_2Cl_6.	$(2 \times 1.8) + (6 \times 6.4) = 42$	42.2
Succinic acid, . . .	$C_4H_6O_4$.	$(4 \times 1.8) + (6 \times 2.3) + (4 \times 4) = 37$	36.9

Thus, *the molecular heat of a compound is the sum of the atomic heats of its elements.**

This law, like the law of Dulong and Petit, of which it is a corollary, is only an approximate law. It generally holds in the case of chlorides, but is an unsafe guide in the case of oxides, especially if the number of atoms in the molecule be large (see page 70); indeed, in some cases, the attempt to deduce the atomic heat of an element from the molecular heat of its oxide has led to fallacious results.

The following table contains the specific and atomic heats of all elements for which the determination has been made. In the case of carbon, silicon, and boron, the values obtained at higher temperatures are employed. The elements are arranged in the order of their atomic weights. The bracketed numbers represent indirect determinations:

* The law of Neumann that the molecular heat of a compound is the sum of the atomic heats of its elements, taken in connection with the fact that the known elements possess an atomic heat approximating to 6.4, has a direct bearing upon the view sometimes advanced that many or all of the known elements are in reality compounds. It is evident either that these supposed compounds do not contain as constituents any of the known elements, since these have already an approximate atomic heat of 6.4, and the resulting "compound" element would necessarily possess a higher atomic heat; or that the mode of combination is totally different from any yet known to chemists. Further, as all the known elements have approximately the same atomic heat, the conclusion appears almost unavoidable, on the "compound" theory, that they are all compounds of exactly the same complexity—containing the same number of constituent atoms, a degree of uniformity which nature does not usually exhibit.

Kundt and Warburg's proof (p. 56) that the molecule of mercury has no internal motion of parts, and is, therefore, in all probability truly monatomic, also appears to militate against the "compound" theory of the elements.

Table of the Specific Heat of the Elements in the Solid State.

Name of element.	Atomic weight.	Specific heat.	Atomic heat.
Hydrogen,	1	(2.3)	(2.3)
Lithium,	7	0.94	6.6
Beryllium (Glucinum),	9	0.45	4.0
Boron,	11	0.5* ?	5.5
Carbon,	12	0.46	5.5
Nitrogen,	14	(0.36)	(5)
Oxygen,	16	(0.25)	(4)
Fluorine,	19	(0.26)	(4.9)
Sodium,	23	0.29	6.7
Magnesium,	24.4	0.25	6.1
Aluminium,	27	0.21	5.7
Silicon,	28.2	0.20	5.6
Phosphorus,	31	0.17	5.3
Sulphur,	32	0.16	5.1
Chlorine,	35.5	(0.18)	6.4
Potassium,	39	0.17	6.6
Calcium,	40	0.17	6.8
Titanium,	48	(0.13)	6.2
Chromium,	52	(0.12)	6.2
Manganese,	55	0.12	6.6
Iron,	56	0.11	6.2
Nickel,	58.6	0.11	6.4
Cobalt,	58.6	0.11	6.4
Copper,	63.2	0.094	5.9
Zinc,	65.3	0.094	6.1
Gallium,	68.8	0.079†	5.4
Arsenic,	75	0.081	6.1
Selenium,	79	0.075	5.9
Bromine,	80	0.084	6.7
Rubidium,	85.3	(0.077)	(6.6)
Strontium,	87.5	(0.074)	(6.5)
Zirconium,	90	0.066	5.9
Molybdenum,	95.5	0.072	6.9
Rhodium,	104	0.058	6.0
Ruthenium,	104	0.061	6.4
Palladium,	105.7	0 059	6.2
Silver,	107.7	0.056	6.0
Cadmium,	112	0.057	6.4
Indium,	113.4	0.057	6.5
Tin,	118	0.056	6.6
Antimony,	120	0.051	6.1
Tellurium,	125	0.047	5 9
Iodine,	127	0.054	6.9
Barium,	137	(0.047)	(6.4)
Lanthanum,	138.5	0.045	6.2
Cerium,	140.5	0.045	6.3
Didymium,	146	0.046	6.7
Tungsten,	184	0.033	6.1
Iridium,	192.5	0.033	6.4
Platinum,	194.4	0.033	6.4
Gold,	196	0 032	6.3
Osmium,	198.6	0.031	6.2
Mercury,	200	0.032	6.4
Thallium,	204	0.034	6.9
Lead,	206.5	0.031	6.4
Bismuth,	208.2	0.031	6.4
Thorium,	233.4	0.028	6.5
Uranium,	238.5	0.028	6.7

* This is a hypothetical value deduced from the experiments of Weber.

† This value was obtained from a determination performed within a limit of eleven degrees—a very narrow range of temperature.

Another mode of expressing the above facts consists in stating what weight of each element has the same capacity for heat as 7 parts by weight of lithium, 7 being the atomic weight of that metal. If the law of Dulong and Petit were a perfectly strict law, the weights which satisfy these conditions would be identical with the atomic weights. In the following table the atomic weights are given side by side with these "specific heat equivalents" in order to indicate clearly in every case the extent of the discrepancy between the two values:

Specific Heat Equivalents of Solid Elements.

Name of element.	Specific heat.	Weights containing equal quantities of heat.	Atomic weight.
Lithium, ...	0.94	7	7
Beryllium (Glucinum), .	0.45	14.6	9
Boron, ...	0.5	13.2	11
Carbon, ...	0.46	14.3	12
Sodium, ...	0.29	22.7	23
Magnesium, ...	0.25	26.3	24.4
Aluminium, ...	0.21	31.3	27
Silicon, ...	0.20	32.9	28.2
Phosphorus, ...	0.17	38.7	31
Sulphur, ...	0.16	41.1	32
Potassium, ...	0.17	38.7	39
Calcium, ...	0.17	38.7	40
Manganese, ...	0.12	54.8	55
Iron, ...	0.11	59.7	56
Nickel, ...	0.11	59.7	58.6
Cobalt, ...	0.11	59.7	58.6
Copper, ...	0.094	70.0	63.2
Zinc, ...	0.094	70.0	65.3
Gallium, ...	0.079	83.3	68.8
Arsenic, ...	0.081	81.2	75
Selenium, ...	0.075	87.7	79
Bromine, ...	0.084	78.3	80
Zirconium, ...	0.066	99.7	90
Molybdenum, ...	0.072	91.4	95.5
Rhodium, ...	0.058	113	104
Ruthenium, ...	0.061	108	104
Palladium, ...	0.059	112	105.7
Silver, ...	0.056	118	107.7
Cadmium, ...	0.057	115	112
Indium, ...	0.057	115	113.4
Tin, ...	0.056	118	118
Antimony, ...	0.051	129	120
Tellurium, ...	0.047	140	125
Iodine, ...	0.054	122	127
Lanthanum, ...	0.045	146	138.5
Cerium, ...	0.045	146	140.5
Didymium, ...	0.046	143	146
Tungsten, ...	0.033	199	184
Iridium, ...	0.033	199	192.5
Platinum, ...	0.033	199	194.4
Gold, ...	0.032	206	196
Osmium, ...	0.031	212	198.6
Mercury, ...	0.032	206	200
Thallium, ...	0.034	194	204
Lead, ...	0.031	212	206.5
Bismuth, ...	0.031	212	208.2
Thorium, ...	0.028	235	233.4
Uranium, ...	0.028	235	238.5

CHAPTER VIII.

CHEMICAL NOTATION. ATOMICITY.

THE use of symbols in place of words, for recording the composition of chemical compounds, and of equations for expressing chemical changes, has long been necessary to accurate description, and has contributed in an important degree to the development of chemistry into an exact science. Unfortunately there has been, and still is, much diversity of opinion amongst chemists as to the best kinds of symbols to be used, and the extent to which these should be employed for expressing the constitution, as well as the composition, of chemical compounds. It would serve no useful purpose and would only confuse the student to review the various systems of notation in actual use amongst chemists, and the description will therefore be here confined to two of those systems, which have been extensively used for many years, and as these systems are based on the doctrine of atomicity, this subject has been introduced into the present chapter.

SYMBOLIC NOTATION.—Every element is represented by a symbol, which is frequently the initial letter of the name of the element; but as, in some cases, the names of two or more elements begin with the same letter, it is necessary to distinguish them by the use of a second letter in small type, which is either the second letter of the word, or some other letter prominently heard in its pronunciation: thus carbon, cadmium, cobalt, and cerium all begin with the same letter; but they are distinguished by the symbols C, Cd, Co, and Ce. In the use of the single letters, the non-metallic elements have the preference; thus oxygen, hydrogen, nitrogen, sulphur, phosphorus, boron, carbon, iodine, and fluorine are expressed by the single letters O, H, N, S, P, B, C, I, and F; whilst the metals osmium, mercury, nickel, strontium, platinum, bismuth, cobalt, iridium, and iron are symbolized by two letters each; thus Os, Hg (hydrargyrum), Ni, Sr, Pt, Bi, Co, Ir, and Fe (ferrum). In the selection of the single letters for other cases, preference is given to the most important element; thus, sulphur, selenium, and silicon are all non-metallic elements, beginning with the same letter; but sulphur being the most important, the single letter S is assigned to it, whilst selenium and silicon are denoted respectively by Se and Si.

The symbols of compounds are formed by the juxtaposition of the symbols of their constituent elements. Such a group of two or more symbols is termed a *chemical formula*. Thus:

Argentic chloride, ...	AgCl.
Zincic oxide, ...	ZnO.

The symbols not only represent the elements for which they are used, but they also denote a certain definite proportion by weight of each element; the formula HCl, for instance, does not merely denote a compound of hydrogen and chlorine, but it signifies a molecule of that compound containing one atom (1 part by weight) of hydrogen, and

one atom (35.5 parts by weight) of chlorine. When, therefore, the molecule of a compound contains more than one atom or combining proportion of any element, it is necessary to express the fact in its formula: this is done by the use of a small subscript coefficient placed after the symbol of the element:

Zincic chloride, ...	$ZnCl_2$.
Ferric chloride, ...	Fe_2Cl_6.
Stannous chloride, ...	$SnCl_2$.
Stannic chloride, ...	$SnCl_4$.

When it is necessary to denote two or more molecules of any compound, a large figure is placed before the formula of the compound; such a figure then affects every symbol in that formula: thus $3SO_4H_2$ means three molecules of the compound SO_4H_2.

The changes which occur during chemical action are expressed by equations, in which the symbols of the elements or compounds, as they exist before the change, are placed on the left, and those which result from the reaction on the right. Thus, taking an example from each of the five kinds of chemical action (see Chemical Affinity) we have

(1) $$Zn + Cl_2 = ZnCl_2.$$
Zinc. Chlorine. Zincic chloride.

(2) $$2HCl + Zn = ZnCl_2 + H_2.$$
Hydrochloric acid. Zinc. Zincic chloride. Hydrogen.

(3) $$SO_4Cu + (NO_3)_2Ba = SO_4Ba + (NO_3)_2Cu.$$
Cupric sulphate. Baric nitrate. Baric sulphate. Cupric nitrate.

(4) $$(CN)O(NH_4) = N_2H_4(CO).$$
Ammonic cyanate. Urea.

(5) $$2OH_2 = O_2 + 2H_2.$$
Water. Oxygen. Hydrogen.

The sign +, as seen from the foregoing examples, is placed between the formulæ of the molecules of the different substances which are brought into contact before the reaction, and of those which result from the change. This sign must never be used to connect together the constituents of one and the same chemical compound.

The sign — is only very rarely used in chemical notation, but when employed it has the ordinary signification of abstraction; thus,

$$SO_4H_2 - OH_2 = SO_3.$$
Sulphuric acid. Water. Sulphuric anhydride.

Use of the Bracket.—The bracket has been employed in various senses in chemical formulæ; but in the present work it is used in notation for one purpose only, viz., for expressing chemical combination between

two or more elements which are placed perpendicularly with regard to each other, and next to the bracket in a formula. Thus in the following cases,

$$\begin{array}{ccc} \text{I.} & \text{II.} & \text{III.} \\ \left\{\begin{array}{l} CH_3 \\ CH_3 \end{array}\right. & \left\{\begin{array}{l} CH_3 \\ O \\ CH_3 \end{array}\right. & \left.\begin{array}{r} NO_2O \\ Ba \\ NO_2O \end{array}\right\} \end{array}$$

the formula No. I. signifies that two atoms of carbon are directly united with each other, No. II. that two atoms of carbon are linked together, as it were, by an atom of oxygen, the latter being united to both carbon atoms; whilst in like manner, No. III. indicates that one atom of oxygen in the formula of the upper line is linked to another atom of oxygen in the formula of the lower line, by an atom of barium.

Use of Thick Letters.—As a rule, the formulæ in this book are so written as to denote that the element represented by the first symbol of a formula is directly united with all the active bonds (see p. 81) of the other elements or compound radicals following upon the same line: thus the formula $\mathbf{S}O_2(OH)_2$ (sulphuric acid) signifies that the hexad atom of sulphur is combined with the four bonds of the two atoms of oxygen, and also with the two bonds of the two semimolecules of hydroxyl. Such a formula is termed a *constitutional formula.**

Occasionally, however, owing to the atomic arrangement of a compound not being known, its formula cannot be written according to this rule; and in order to prevent such formulæ, whether *molecular* or *empirical*,† from being mistaken for constitutional formulæ, the first symbol of a constitutional formula will always be printed in thick type. As a rule, the element having the greatest number of bonds will occupy this prominent position. Thus:

Sulphuric acid, ...	$\mathbf{S}O_2(OH)_2$.
Water, ...	$\mathbf{O}H_2$.
Nitric acid, ...	$\mathbf{N}O_2(OH)$.
Microcosmic salt, ...	$\mathbf{P}O(OH)(ONH_4)(ONa)$.

* For further information on this subject see ATOMICITY OF ELEMENTS and COMPOUND RADICALS.

† A *molecular formula*, sometimes called *rational*, is one in which the atomic composition of a molecule is expressed, but without reference to the manner in which the elements are combined amongst themselves. An *empirical formula* merely expresses, by the smallest integers, the proportional number of atoms of each element entering into the composition of a compound. Thus the three formulæ of ferric hydrate are written:

Empirical formula, ...	FeH_3O_3.
Molecular formula, ...	$Fe_2H_6O_6$.
Constitutional formula, ...	$\mathbf{Fe}_2(OH)_6$.

Constitutional or rational formulæ are therefore essentially molecular formulæ, whilst empirical formulæ afford no indication of the number of atoms contained in a molecule; they are, in fact, only used to express the composition of substances, the molecular weights of which are either unknown or cannot be inferred from analogy.

Atomicity of Elements.

It has been already stated that the atomic weight of an element is the smallest proportion by weight in which that element enters into or is expelled from a chemical compound. The atoms of the various elements, the relative weights of which are thus expressed, possess very different values in chemical reactions. Thus, an atom of zinc is equivalent to two atoms of hydrogen, for when zinc is brought into contact with steam at a high temperature, one atom of zinc expels from the steam two atoms of hydrogen, and occupies their place, thus:

$$\underset{\text{Water.}}{OH_2} + Zn = \underset{\text{Zincic oxide.}}{OZn} + H_2.$$

Again, when zincic oxide is brought into contact with hydrochloric acid, the place of the zinc becomes once more occupied by hydrogen, but two atoms of hydrogen are found to be necessary to take the place of one atom of zinc:

$$\underset{\substack{\text{Zincic}\\ \text{oxide.}}}{OZn} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl} = \underset{\substack{\text{Zincic}\\ \text{chloride.}}}{ZnCl_2} + \underset{\text{Water.}}{OH_2}.$$

In like manner, one atom of boron can be substituted for three atoms of hydrogen, one of carbon for four, one of nitrogen for five, and one atom of sulphur for no fewer than six atoms of hydrogen.

This combining value of the elementary atoms, which was first discovered in the compounds of certain metals with organic radicals, is termed their *atomicity*, *equivalence*, *valency*, or *atom-fixing power;* and an element, with an atom-fixing power equal to that of one atom of hydrogen is termed a *monad*, one with twice that power a *dyad*, with thrice a *triad*, with quadruple a *tetrad*, with quintuple a *pentad*, and with an atom-fixing power equal to six times that of hydrogen, a *hexad*.

To avoid any speculation as to the nature of the tie which enables an element thus to attach to itself one or more atoms of other elements, each unit of atom-fixing power will be named a *bond*,—a term which involves no hypothesis as to the nature of the connection. A monad element has, obviously, only one such bond; a dyad, like zinc, two; a triad, like boron, three, and so on. The number of bonds possessed by an elementary atom may be usefully symbolized by lines in the following manner:

Hydrogen, ... H—

Zinc, ... —Zn—

Boron, ... $\diagdown\diagup$ B $|$

Carbon, ... $-\overset{|}{\underset{|}{C}}-$

Nitrogen, ... 

Sulphur, ... 

In symbolic notation, the same idea is conveyed by the use of dashes and Roman numerals placed above and to the right of the symbol of the element, thus:

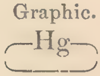
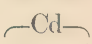
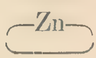
Hydrogen, . . .	H',	Carbon, . . .	C^{iv},
Zinc, ...	Zn'',	Nitrogen, . .	N^{v},
Boron, ...	B''',	Sulphur, . .	S^{vi}.

Elements with an odd number of bonds are termed *perissads*, whilst those with an even number are named *artiads.*

With very few exceptions, elements, either alone or in combination, are never found to exist with any of their bonds free or disconnected; hence, *the molecules of all elements with an odd number of bonds are generally diatomic, and always polyatomic;* that is, they contain two or more atoms of the element united together. Thus:

	Symbolic.	Graphic.
Hydrogen, ...	H_2	H—H
Chlorine, ...	Cl_2	Cl—Cl
Nitrogen, ...	N^{v}_2	N≡N
Phosphorus, ...	P^{v}_4	P═P ||| ||| P═P

An element, with an even number of bonds, however, can exist as a monatomic molecule, its own bonds apparently satisfying each other. Thus:

	Symbolic.	Graphic.
Mercury, ...	Hg''	
Cadmium, ...	Cd''	
Zinc, ...	Zn''	

It is, nevertheless, obvious that such an element may also exist as a polyatomic molecule. Oxygen furnishes us with an example of this; for, in its ordinary condition, it is a diatomic molecule, and, in the allotropic form of ozone, a triatomic molecule:

	Symbolic.	Graphic.
Oxygen, ...	O''_2	O═O
Ozone, ...	O''_3	

In order to avoid the unnecessary use of atomicity-marks in symbolic notation, they will never be attached to a monad, or to oxygen, which, it must be remembered, is always a dyad. Neither will the atomicity coefficient be attached to the tetrad element carbon, in the formulæ of organic bodies, unless this element plays the part of a dyad, an occurrence of extreme rarity. When not otherwise marked, therefore, carbon must always be understood to be a tetrad.

It will also, as a rule, be unnecessary to mark the atomicity of the elements which are expressed by symbols in thick type, because their atomicity is clearly indicated by the sum of the atomicities of the elements or compound radicals placed to their right, or connected with them perpendicularly by a bracket. Thus, in the formula

$$\begin{cases} \mathbf{C}Cl_3, \\ \mathbf{C}Cl_3, \end{cases}$$

each atom of carbon is united with three atoms of the monad chlorine, whilst the bracket indicates that the two atoms of carbon are also united by one bond of each, thus denoting **C** to be a tetrad element.

From what has just been said with regard to carbon, it is evident that the atomicity of an element is, apparently at least, not a fixed and invariable quantity; thus, nitrogen is sometimes equivalent to five atoms of hydrogen, as in ammonic chloride ($\mathbf{N}^{v}H_4Cl$), sometimes to three atoms, as in ammonia ($\mathbf{N}'''H_3$), and sometimes to only one atom, as in nitrous oxide ($\mathbf{O}N_2$). But it is found that this variation in atomicity takes place, with very few exceptions, by the disappearance or development of an even number of bonds; thus, nitrogen, except in nitric oxide (NO), and dissociated nitric peroxide (NO_2), is either a pentad, a triad, or a monad; phosphorus and arsenic, either pentads or triads; carbon and tin, either tetrads or dyads; and sulphur, selenium, and tellurium, either hexads, tetrads, or dyads.

These remarkable facts can be explained by a very simple and obvious assumption, viz.: *That one or more pairs of bonds belonging to the atom of an element can unite, and, having saturated each other, become, as it were, latent.* Thus, the pentad element, nitrogen, becomes a triad when one pair of its bonds becomes latent, and a monad, when two pairs, by combination with each other, are, in like manner, rendered latent,—conditions which may be graphically represented thus:

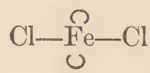
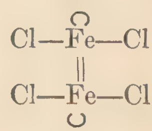
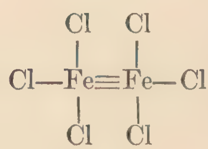
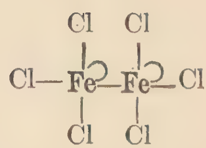
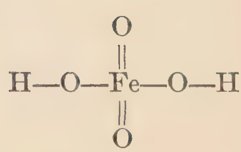
Pentad. Triad. Monad.

And in the case of sulphur:

Hexad. Tetrad. Dyad.

Adopting this hypothesis, it will be convenient to distinguish the maximum number of bonds of an element as its *absolute atomicity*, the number of bonds united together as its *latent atomicity*, and the number of bonds actually engaged in linking it with the other elements of a compound as its *active atomicity*. The sum of the active and latent atomicities of any element must evidently always be equal to the absolute atomicity. Thus in sulphuric acid ($\mathbf{S}^{vi}O_2Ho_2$) the absolute and active atomicities are both = VI, therefore the latent atomicity = 0. In sulphurous acid ($''\mathbf{S}^{iv}OHo_2$) the active atomicity = IV, and consequently the latent = VI — IV = II; whilst in sulphuretted hydrogen (${}^{iv}\mathbf{S}''H_2$) the active and latent atomicities are respectively II and IV.

The apparent exceptions to this hypothesis nearly all disappear on investigation. Thus iron, which is a dyad in ferrous compounds (as $\mathbf{Fe}Cl_2$), a tetrad in iron pyrites ($\mathbf{Fe}S''_2$), and a hexad in ferric acid ($\mathbf{Fe}O_2(OH)_2$), is apparently a triad in ferric chloride ($\mathbf{Fe}Cl_3$); but the vapor-density of ferric chloride shows that its formula must be doubled —that, in fact, the two atoms of the hypothetical molecule of iron (Fe_2) have not been completely separated. The formulæ of the ferrous and ferric chlorides and of ferric acid then become

	Symbolic.	Graphic.
Ferrous chloride, . .	${}^{iv}\mathbf{Fe}''Cl_2$	
or	$''\left\{\begin{matrix}''\mathbf{Fe}Cl_2\\ ''\mathbf{Fe}Cl_2.\end{matrix}\right.$	
Ferric chloride, ...	$'''\mathbf{Fe}'''_2Cl_6$	
or	$\left\{\begin{matrix}''\mathbf{Fe}Cl_3\\ ''\mathbf{Fe}Cl_3.\end{matrix}\right.$	
Ferric acid, . . .	$\mathbf{Fe}^{vi}O_2(OH)_2.$	

It will be remarked that the number of bonds supposed to be combined with each other in the atom of iron in ferrous chloride is expressed

in one of the above formulæ by the atomicity numeral IV placed to the left of the symbol, whilst the analogous union of three bonds of each atom of iron in ferric chloride is expressed by the three dashes ''' to the left of the symbol $\mathbf{Fe}_2$. These coefficients of latent atomicity will not, however, be used in the case of the single atom of an element, the student being supposed to have made himself acquainted with the absolute atomicity of every element, as expressed in the Table given in Chap. X. For a similar reason it will also rarely be necessary to express the same idea in graphic notation. Thus, for instance, ammonia will be drawn

$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—N—H} \end{array} \qquad \text{and not} \qquad \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—N—H} \\ \circ \end{array}$$

It will be necessary, however, to employ these coefficients in symbolic formulæ where two or more atoms of the same element are joined together under such circumstances that the number of bonds uniting them cannot be found by subtracting the coefficient of active atomicity from the absolute atomicity of the element, as in hydric persulphide ($'\mathbf{S}'_2\mathrm{H}_2$), for instance, which might otherwise be viewed as $'''\mathbf{S}'_2\mathrm{H}_2$, or $^{\mathrm{v}}\mathbf{S}'_2\mathrm{H}_2$.

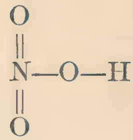
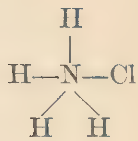
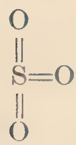
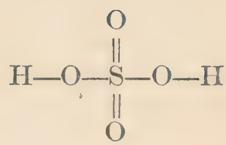
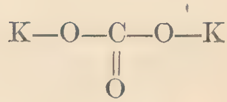
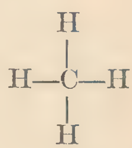
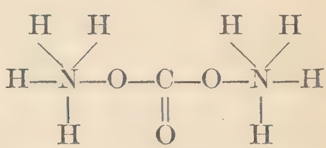
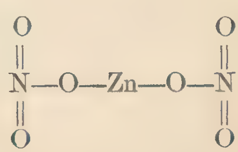
In rare cases, in which oxygen links together two elements or radicals in the same line of a formula, a hyphen is placed before and after the symbol O, thus;

$$\left\{\begin{array}{l} \mathbf{C}\mathrm{H_2\text{-}O\text{-}}\mathbf{C}\mathrm{MeO} \\ \mathbf{C}\mathrm{H_2\text{-}O\text{-}}\mathbf{C}\mathrm{MeO}\cdot \end{array}\right.$$

Diacetic glycol.

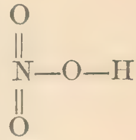
GRAPHIC NOTATION.—This mode of notation, although far too cumbrous for general use, is invaluable for clearly showing the arrangement of the individual atoms of a chemical compound. It is true that it expresses nothing more than the symbolic notation of the same compound, if the latter be written and understood as above described; nevertheless the graphic form affords most important assistance, both in fixing upon the mind the true meaning of symbolic formulæ, and also in making comparatively easy of comprehension the probable internal arrangement of the very complex molecules frequently met with both in mineral and organic compounds. It is also of especial value in rendering strikingly evident the causes of isomerism in organic bodies; and it is now almost universally employed by chemists in describing the results of their new discoveries.

Graphic notation, like the above method of symbolic notation, is founded essentially upon the doctrine of atomicity, and consists in representing graphically the mode in which every bond in a chemical compound is disposed of. Inasmuch, however, as the principles involved are precisely the same as those already described under the heads of SYMBOLIC NOTATION and ATOMICITY OF ELEMENTS, it is unnecessary here to do more than give the following comparative examples of symbolic and graphic formulæ:

	Symbolic.	Graphic.
Water, ...	OH_2.	H—O—H
Nitric acid, . . .	$NO_2(OH)$.	
Ammonic chloride,	NH_4Cl.	
Sulphuric anhydride,	SO_3.	
Sulphuric acid, . .	$SO_2(OH)_2$.	
Carbonic anhydride,	CO_2.	O=C=O
Potassic carbonate, .	$CO(OK)_2$.	
Marsh-gas, . . .	CH_4.	
Ammonic carbonate,	$CO(ONH_4)_2$.	
Zincic nitrate, . .	$\left.\begin{array}{l}NO_2O\\ \quad Zn''\\ NO_2O\end{array}\right\}$	

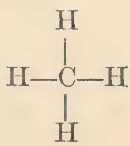
It must be carefully borne in mind that these graphic formulæ are intended to represent neither the shape of the molecules, nor the sup-

posed relative position of the constituent hypothetical atoms. The lines connecting the different atoms of a compound, and which might with equal propriety be drawn in any other direction, provided they connected together the same elements, serve only to show the definite disposal of the bonds, the latter again being only a concrete symbolic expression of an abstract train of reasoning; thus the formula for nitric acid indicates that two of the three constituent atoms of oxygen are combined with nitrogen alone, and are consequently united to that element by both their bonds, whilst the third oxygen atom is combined both with nitrogen and hydrogen.

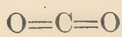


The lines connecting the different atoms of a compound are but crude symbols of the bond of union between them; and it is scarcely necessary to remark that no such material connections exist, the bonds which actually hold together the constituents of a compound being, as regards their nature, entirely unknown.

It deserves also to be here mentioned that graphic, like symbolic formulæ, are purely statical representations of chemical compounds: they take no cognizance of the amount of potential energy associated with the different elements. Thus in the formulæ for marsh-gas and carbonic anhydride,



Marsh-gas.



Carbonic anhydride.

there is no indication that the molecule of the first compound contains a vast store of force, whilst the last is, comparatively, a powerless molecule.

Calculation of Formulæ.—By quantitative analysis the relative weights of the various constituents of a compound body are discovered, and these relative weights are usually expressed in parts per 100. From these numbers the formula of the compound has to be calculated. The percentage composition expresses the relative proportions of the component elements in terms of a common unit; in the formula, the proportion of each element is expressed in terms of its atomic weight. In order, therefore, to ascertain in what proportion of their atomic weights the elements occur in the compound, it is only necessary to divide the proportion of each element in 100 parts of the compound by the atomic weight of that element. Thus the analysis of acetic acid yields the following percentage composition:

	In 100 *parts.*
Carbon,	40.00
Hydrogen,	$6.6\dot{6}$
Oxygen,	$53.3\dot{3}$
	$99.9\dot{9}$

Dividing each of these numbers by the atomic weight of the element in question, we find: $\frac{40.00}{12} = 3.33$; $\frac{6.66}{1} = 6.66$; and $\frac{53.33}{16} = 3.33$. Therefore the atomic proportion of carbon : hydrogen : oxygen in acetic acid is as 3.33 : 6.66 : 3.33, or as 1 : 2 : 1. The formula of acetic acid would thus be CH_2O.

This is, however, only the empirical formula, or smallest possible proportion of the atomic weights. We have already seen (p. 60) that the molecular formula of acetic acid is $C_2H_4O_2$, or twice as great as the above.

CHAPTER IX.

COMPOUND RADICALS.

THE term compound radical may be applied to any group of two or more atoms, which takes the place and performs the functions of an element in a chemical compound. In practice, however, it is only applied to any such group when met with in numerous chemical compounds.

An element is a *simple radical,* and enters into combination in the following manner, a, b, c, and d being monad elements, a'' a dyad, a''' a triad, and a^{iv} a tetrad element:

$$\begin{aligned} a' &+ b = ab, \\ a'' &+ 2b = a''b_2, \\ a''' &+ 3b = a'''b_3, \\ &\text{etc.} \qquad \text{etc.} \end{aligned}$$

A group of elements replacing a, a'', or a''' in the above equations is a *compound radical,* as in the following examples:

$$\begin{aligned} (a''b) &+ b = (a''b)b, \\ (a'''b)'' &+ 2b = (a'''b)''b_2, \\ (a'''bc) &+ b = (a'''bc)b, \\ (a^{\text{iv}}b)''' &+ 3b = (a^{\text{iv}}b)'''b_3, \\ (a^{\text{iv}}bc)'' &+ 2b = (a^{\text{iv}}bc)''b_2, \\ (a^{\text{iv}}bcd) &+ b = (a^{\text{iv}}bcd)b. \end{aligned}$$

The group of elements $(a''b)$ constitutes a compound monad radical equivalent to one atom of hydrogen or chlorine. The group $(a'''b)''$ is a compound dyad radical, etc. It is therefore evident that a polyad element is essential to every compound radical; in fact *a compound radical consists of one or more atoms of a polyad element in which one or more bonds are unsatisfied; and it is either a monad, dyad, triad, etc., radical, according to the number of monad atoms required to satisfy its active atomicity.* Such a radical, when a monad, triad, or pentad, cannot exist as a separate group: like hydrogen or nitrogen, when isolated, it combines with itself, forming a duplex molecule. It is only by the

union of two atoms or groups of atoms that the vacated bonds can in these cases be satisfied.

From the above definition of a compound radical, it is evident that an almost infinite number of such bodies must exist; for in the compounds of every polyad element it is only necessary to vacate successive bonds to create each time a new compound radical. Thus marsh-gas CH_4 minus one atom of hydrogen gives the compound radical methyl CH_3; minus two atoms of hydrogen, it forms methylene $(CH_2)''$; and by the abstraction of three hydrogen atoms it is transformed into the triad radical formyl $(CH)'''$; but, except in a few cases, it is not advantageous thus to incorporate, as it were, compound radicals, which, instead of simplifying notation and nomenclature, would, if thus multiplied, only embarrass them. No compound radical, therefore, ought to receive recognition as such, unless it can be shown to enter into the composition of a large number of compounds.

The following are the names, symbols, and formulæ of the inorganic compound radicals recognized in the notation of this volume:

	Molecular formulæ.	Semimolecular formulæ.	Semimolecular symbols.
Hydroxyl, ...	$(OH)_2$	OH	Ho.
Hydrosulphyl, . . .	$(SH)_2$	SH	Hs.
Ammonium, ...	$(NH_4)_2$	NH_4	Am.
Ammonoxyl, ...	$(ONH_4)_2$	ONH_4	Amo.
Amidogen, ...	$(NH_2)_2$	NH_2	Ad.

In addition to these, certain compounds which metals form with oxygen are also regarded as compound radicals—for instance,

	Molecular formulæ.	Semimolecular formulæ.	Semimolecular symbols.
Potassoxyl, . .	$(OK)_2$	OK	Ko.
Zincoxyl, . . .	(O_2Zn)	$\left\{\begin{matrix}O\\Zn''\\O\end{matrix}\right.$	Zno''.

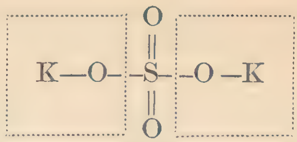
The essential character of these last compound radicals is that the whole of the oxygen they contain is united with the metal by one bond only of each oxygen atom, as seen in the following graphic formulæ:

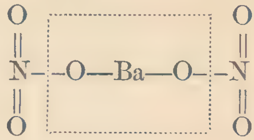
Hydroxyl, ...	—O—H
Potassoxyl, ...	—O—K
Zincoxyl, ...	—O—Zn—O—

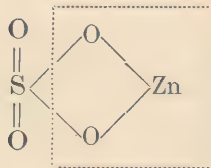
The metal thus becomes linked to other elements by these dyad atoms of oxygen. The functions of such compound radicals will be sufficiently evident from the following examples of compounds into which they enter, and in which their position is marked by dotted lines.

Nitric acid, ...

$$\begin{array}{l} O \\ \| \\ N-\boxed{-O-H} \\ \| \\ O \end{array}$$

Potassic sulphate, . 

Baric nitrate, . . 

Zincic sulphate, . . 

It is not necessary to dignify all these metallic compound radicals with names; the chief point of importance about them is their abbreviated notation, in which the small letter o is attached to the symbol of the metal, the atomicity of the radical being marked in the usual manner. Although the small letter o in these symbols of combining quantities has no more reference to the composition of the radical than the d in the corresponding symbol of amidogen, yet it may usefully remind the reader that oxygen is always a constituent of the compound radicals so symbolized. It must be borne in mind that the number of atoms of oxygen in any radical of this class depends upon its atomicity: thus a monad contains only one atom of oxygen, a dyad two, and a triad always three atoms of oxygen. The use of any but monad and dyad metallic compound radicals is very rare.

It is also in some cases convenient to recognize as a radical the atomic group which remains when all the hydroxyl is abstracted from an oxyacid, as for instance:

Acid.		Acid radical.	
Nitrous acid, ...	$\mathbf{NOHo}$	Nitrosyl, ...	(NO)
Nitric acid, ...	$\mathbf{NO_2Ho}$	Nitroxyl, ...	(NO_2)
Sulphuric acid, . . .	$\mathbf{SO_2Ho_2}$	Sulphuryl, . . .	$(SO_2)''$
Phosphoric acid, . .	$\mathbf{POHo_3}$	Phosphoryl, . . .	$(PO)'''$

It is evident that the atomicity of these elements must be the same as the basicity of the acids from which they are derived.

Atomic and Molecular Combination.

In all the cases of chemical combination already considered, a union of atoms has been invariably contemplated. This atomic union is generally attended by the breaking up of previously existing molecules—two such molecules, by the mutual exchange of their atomic constituents, producing two new and perfectly distinct molecules. Thus, when chlorine unites with hydrogen to form hydrochloric acid, a molecule of

chlorine and one of hydrogen yield up their constituent atoms, forming two molecules of hydrochloric acid,

$$Cl_2 + H_2 = 2HCl.$$

In comparatively rare cases, two molecules combine to form only one new molecule; thus a molecule of carbonic oxide and one of chlorine combine to form one melecule of carbonic oxydichloride or phosgene gas: but the union is even here essentially atomic; for after combination both the oxygen and chlorine are directly united with the atom of carbon:

$\mathbf{C}''O$	+	Cl_2	=	$\mathbf{C}^{iv}OCl_2$.
Carbonic oxide.		Chlorine.		Phosgene gas.

Chemists are, however, compelled to admit an entirely different kind of union, which not unfrequently occurs, and which in conformity with the atomic hypothesis, may be appropriately termed *molecular union* or *molecular combination.* In the formation of such compounds, no change takes place in the active atomicity of any of the molecules. It is this kind of combination which holds together salts and their water of crystallization, as, for instance,

Sodic chloride crystallized at	— 10° C., . .	$NaCl,2\mathbf{O}H_2$.
Sodic bromide crystallized below	+ 30° C., . .	$NaBr,2\mathbf{O}H_2$.
Sodic iodide crystallized below	+ 50° C., . .	$NaI,2\mathbf{O}H_2$.
Alum, ...		$\mathbf{S}_4O_8('Al'''_2O_6)^{vi}Ko_2,24\mathbf{O}H_2$.

Numerous other instances of molecular combination might be adduced; but it is only necessary here to point out that such molecular unions will be distinguished from atomic combinations by the use of the comma, as in the above and following examples:

Tetramethylammonic tri-iodide, . . .	$\mathbf{N}Me_4I,I_2$.
Tetramethylammonic pentiodide, . . .	$\mathbf{N}Me_4I,2I_2$.
Tetramethylammonic iodo-dichloride, . .	$\mathbf{N}Me_4I,Cl_2$.

In all cases molecular combination seems to be of a much more feeble character than atomic union; for, in the first place, such bodies are generally decomposed with facility; and secondly, the properties of their constituent molecules are markedly perceptible in the compounds. Thus the above periodides of the organic bases greatly resemble iodine in appearance.

CHAPTER X.

CLASSIFICATION OF ELEMENTS.

It has been already mentioned that the elements may be divided into two great classes, the metals and the non-metals or metalloids. A second division into positive and negative elements has also been explained. A third and still more important classification is founded upon the atomicity of the elements. In the following classified table, all three methods are embodied, the names of the metalloids being printed in heavy type, and those of the metals in common type, whilst the names of the positive elements are printed in Roman characters,

and those of the negative in italics. In addition, the different classes are also divided into sections, consisting of elements closely related in their chemical characters.

Monads.	Dyads.	Triads.	Tetrads.	Pentads.	Hexads.	Heptads.	Octads.
1st Section. **Hydrogen.**	1st Section. ***Oxygen.***	1st Section. **Boron.**	1st Section. **Carbon.** **Silicon.** Titanium. Zirconium. Tin. Thorium.	1st Section. **Nitrogen.** **Phosphor's** Vanadium. Arsenic. Niobium. Antimony. Tantalum. Bismuth.	1st Section. ***Sulphur.*** ***Selenium.*** ***Tellurium.***	***Chlorine*** ***Bromine*** ***Iodine.*** (?)*	Ruthenium. Osmium.
2d Section. ***Fluorine.*** ***Chlorine.*** ***Bromine.*** ***Iodine.*** (?)*	2d Section. Barium. Strontium. Calcium. Magnesium. Zinc. Beryllium.	2d Section. Gold.	2d Section. Gallium. Aluminium.	2d Section. Didymium.	2d Section. Uranium. Tungsten. Molybdenum.		
3d Section. Cæsium. Rubidium. Potassium. Sodium. Lithium.	3d Section. Cadmium. Mercury. Copper.	3d Section. Thallium. Indium.	3d Section. Cerium.		3d Section. Chromium. Manganese. Iron. Cobalt. Nickel.		
4th Section. Silver.		4th Section. Lanthanum. Yttrium. Erbium. Decipium. Samarium. (?) Scandium.	4th Section. Platinum. Iridium. Palladium. Rhodium.				
			5th Section. Lead.				

* Chlorine, bromine, and iodine have been treated as monadic in the present work; but in the opinion of some chemists these elements are heptadic (see "Periodates").

Classification of the Elements according to their Atomic Weights.—The Periodic Law.—The idea of a possible connection between the atomic weights of the elements and their properties was first suggested by the observation that in many cases similar elements could be arranged in groups of three, in which the atomic weight of the intermediate element was approximately the arithmetical mean of the atomic weights of the highest and lowest. Examples of such groups, which were termed "triads," are

$$P = 31, As = 75, Sb = 120 — \quad \frac{31 + 120}{2} = 75.5.$$

$$Cl = 35.5, Br = 80, I = 127 — \quad \frac{35.5 + 127}{2} = 81.25.$$

$$Ca = 40, Sr = 87.5, Ba = 137 — \quad \frac{40 + 137}{2} = 88.5.$$

The most complete expression of these relations that has yet been proposed is to be found in the "periodic law of the elements."

The fact that the properties of the elements vary periodically with their atomic weights was first shown by Newlands in 1864.* More complete and systematic expressions of the same law were published a few years later by Mendeleef and by Lothar Meyer. The most precise of these systems is that of Mendeleef, which has lately attracted much attention on account of the number of new facts which it has enabled its author to predict. The following is a brief outline of the method followed by Mendeleef.

If all the elements whose atomic weights lie between 7 and 35.5 be arranged in the arithmetical order of their atomic weights, thus:

$$Li = 7;\ Be = 9.4;\ B = 11;\ C = 12;\ N = 14;\ O = 16;\ F = 19;$$
$$Na = 23;\ Mg = 24;\ Al = 27.3;\ Si = 28;\ P = 31;\ S = 32;\ Cl = 35.5,$$

certain definite relations may be perceived. The character of the elements is here seen to be subject to regular modification, so that, step by

* Newlands was the first to point out that the elements, when arranged in the arithmetical order of their atomic weights, exhibit a periodic recurrence of similar properties. He stated that each such period consists of seven elements, and that, with the eighth element, properties resembling those of the first recur. To this relation he gave the name of the *Law of Octaves*, comparing the periods of recurrence with the octaves of the musical scale, and the elements within the period with the notes included in the octave. Newlands's system is therefore in all essential points identical with that of Mendeleef, which was published in 1869; except that Newlands failed to recognize the existence of the "transitional elements"—Mendeleef's eighth group (see table, p. 92)—which divide the other elements into groups of two octaves each.

The fact that Mendeleef's table, published five years later than the first table given by Newlands, is undoubtedly more perfect in its details, has led some chemists to ascribe the discovery of the periodic law to the former investigator. This is manifestly unjust. The credit of originating an idea is due solely to him who first formulates it, and this is irrespective of any subsequent development which the idea may undergo at the hands of others, provided that the central idea itself remains unaltered. No one, for example, has ever suggested that the authorship of the modern atomic theory is to be ascribed to Cannizzaro instead of to Dalton, because the rectification of the atomic weights was the work of the former chemist.

step, as the atomic weights vary, the characters of the elements also vary, and by comparing the series of elements from Li to F with the series from Na to Cl, it is manifest that this variation is a periodic one, the same changes of character which are met with in traversing the first series, being again found in the second series: thus Li corresponds to Na, Be to Mg, B to Al,* etc. The regularity of the change in traversing a period may be seen by comparing with each other the oxides of one such series of elements, writing these so as to show the relative quantities of oxygen with which the same number of atoms of the various elements combine, instead of employing the molecular formulæ of the oxides:

$$\underset{}{Na_2O};\ \underset{(MgO)}{Mg_2O_2};\ Al_2O_3;\ \underset{(SiO_2)}{Si_2O_4};\ P_2O_5;\ \underset{(SO_3)}{S_2O_6};\ Cl_2O_7.\dagger$$

Here the proportion of oxygen in the various oxides throughout the period is as 1 : 2 : 3 : 4 : 5 : 6 : 7. At the same time there is a regular gradation from left to right from the most electropositive element, through the various intermediate stages, to the most electronegative element. This periodic recurrence of the same properties with the gradual increase of the atomic weight has been formulated by Mendeleef thus: *The properties of the elements are a periodic function of their atomic weights.*

Following out this principle, Mendeleef has tabulated the whole of the elements on the same plan (see table, page 92).

The Roman numerals indicate the *groups* or families of similar elements, which are thus arranged in vertical columns; the Arabic numerals refer to the *series* or periods, which are arranged horizontally. As regards the latter, it is to be noted that there are two kinds of periods—the one following the even Arabic numerals, the other the odd. If we confine our attention to a single group, we find that the elements of the even periods correspond with each other in their properties, and that the elements of the odd periods likewise correspond with each other, but that there is less correspondence of the members of one of these classes with those of the other. Thus, in Group II., the corresponding elements of the even series are Be, Ca, Sr, and Ba; of the odd series, Mg, Zn, Cd, and Hg.

The series 2 and 3 are termed by Mendeleef "short periods"; the remaining series are grouped together in pairs—thus, 4 and 5, 6 and 7, 8 and 9, etc.—the two series of such a pair together constituting a "long period." That is to say, if we traverse the series 3 we find a periodic repetition of the chemical characteristics already met with in series 2; but in order to meet with a similar periodic change of characteristics—*e. g.*, in order to pass from a highly electropositive to a highly electronegative element—it is necessary to traverse the entire *double*-series 4 and 5, and again the double-series 6 and 7, and so on. The full significance of this arrangement—at first sight, perhaps a somewhat arbitrary one—will be shown further on.

* On this supposition Al would have to be regarded as triadic. This would be in harmony with the observed vapor-density of aluminic methide, $Al(CH_3)_3$, at 240°.

† Perchloric anhydride is not known; but the corresponding acid has been prepared.

The Periodic System of the Elements.

Groups:	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series:	— R_2O	— R_2O_2	— R_2O_3	RH_4 R_2O_4	RH_3 R_2O_5	RH_2 R_2O_6	RH R_2O_7	(R_2H) (R_2O_8)
1 2	1 H Li 7	— Be 9	— B 11	— C 12	— N 14	— O 16	— F 19	— —
3 4	23 Na K 39	24.4 Mg Ca 40	27 Al Sc 44	28.2 Si Ti 48	31 P V 51.3	32 S Cr 52	35.5 Cl Mn 55	Fe 56, Co 58.6, Ni 58.6
5 6	63.2 Cu Rb 85.3	65.3 Zn Sr 87.5	68.8 Ga Y 89.8 ?	72 ? Zr 90	75 As Nb 94	79 Se Mo 95.5	80 Br ? 100	Ru 104, Rh 104, Pd 105.7
7 8	107.7 Ag Cs 133	112 Cd Ba 137	113.4 In La 138.5	118 Sn Ce 140.5	120 Sb Di 146	125 Te Tb? 148.8	127 I Sm? 150	? 152, ? 153, ? 154
9 10	156 ? ? 170	158 ? ? 172	159 Dp? Yb 172.8	162 ? ? 177	165.9 Er? Ta 182	167 ? W 184	169 ? ? 190	Os 198.6 ?, Ir 192.5, Pt 194.4
11 12	196 Au ? 221	200 Hg ? 225	204 Tl ? 230	206.5 Pb Th 233.4	208.2 Bi ? 237	214 Ng? U 238.5	219 ? ? 244	

In passing from the left to the right there is in every series, taking each group in that series in succession, a gradual increase in the quantity of oxygen with which the elements can unite. The members of the different groups taken in order exhibit a regular change (generally an increase) of atomicity, odd and even atomicities alternating. Group VIII. is anomalous. In this group there are always three elements in each series, instead of, as in the other groups, only one element. These elements of Group VIII. do not, when taken in any series in the order of their atomic weights, exhibit the above alternation of odd and even atomicity: they are all even; but their atomicity decreases with a rise of atomic weight. They are termed by Mendeleef "transitional elements," and their place is between the even and the odd series of a long period. This transitional group will be referred to again later on.

The grouping together of sodium, silver, and copper as similar elements is justified by the isomorphism of some of the cuprous and argentic compounds, and of some of the latter again with the corresponding sodium compounds.

Mendeleef has employed this periodic law in the correction of doubtful atomic weights, and in the prediction of undiscovered elements.

Thus, indium was formerly believed to be a dyad with the atomic weight 76, and its oxide was therefore supposed to possess the formula InO. With this atomic weight, it would take its place between arsenic and selenium. But there is no vacant space for it in this part of the table, and it would, moreover, have no analogy with the elements with which it would have to be grouped. Mendeleef pointed out that by assuming indic oxide to possess the formula In_2O_3, with an atomic weight for the metal of 114, indium would take its place in series 7 between cadmium and tin, and as an analogue of aluminium. The correctness of this view has been demonstrated by the determination of the specific heat of indium by Bunsen.

Again, chemists were uncertain whether uranium had the atomic weight 60 or 120. Mendeleef showed that no element of either of these atomic weights and of the properties of uranium would find a fitting place in the table, but that by assigning to it the atomic weight 240 (238.5), it would take its place as an analogue of chromium, molybdenum, and tungsten. This change has been justified by the results of the determination of the specific heat of uranium and by the vapor-density of various uranium compounds.

Again, the determinations of the atomic weight of molydenum left it uncertain whether this element possessed the atomic weight 92 or 96. The former of these weights would place it before niobium, and in a group of elements with which it presents no analogy. In order that it might take its place in Group VI. as an analogue of chromium, its atomic weight must be higher than 94, the atomic weight of niobium. A careful determination has in fact shown that the atomic weight of molybdenum is 95.5.

Again, tellurium was supposed to have the atomic weight 128. In order that it might take its place in the same group as its chemical analogues sulphur and selenium, it was necessary that its atomic weight

should be lower than 127, the atomic weight of iodine. A recent determination by improved methods has shown that the atomic weight of tellurium is 125.

It will be noticed that in the foregoing table one element, osmium, has been placed in a position different from that indicated by its atomic weight as at present determined. Osmium from its properties ought to have an atomic weight lower than that of iridium, instead of higher than that of gold. It remains to be seen whether experiment will, as in the preceding cases, verify this prediction.

Mendeleef has shown that the properties, both chemical and physical, of an element may be to a certain extent predicted from the properties of what he terms its "atomic analogues." By this term he understands not its chemical analogues, but the two elements which stand on either side of it in the same series, together with the two elements which stand above and below it in the same group. Thus As, Br, S, and Te are the atomic analogues of Se.

It will be observed that there are in the table a number of gaps. These correspond, according to Mendeleef, with elements which have not yet been discovered. If such a gap is surrounded by the requisite atomic analogues, it is possible to predict the properties of the unknown element. Thus in the positions III. 4, III. 5, and IV. 5, Mendeleef placed three unknown elements to which he gave the names *ekaboron*, *ekaluminium*, and *ekasilicon*—following a system of nomenclature which he has devised for the designation of such unknown elements and which, while referring these to known elements of the same group, distinguishes them by prefixing the Sanscrit numerals *eka*, *dvi*, *tri*, etc., according to their position in the group. Concerning ekaluminium, he states that it has an atomic weight of about 68, and a specific gravity of about 6.0, and that it forms a sesquioxide. These predictions were verified by the discovery of gallium, which has an atomic weight of 68.8, a specific gravity of 5.9, and forms an oxide of the formula Ga_2O_3. The new metal scandium is possibly Mendeleef's ekaboron.

The above prediction of the specific gravity of ekaluminium (gallium) is rendered possible by the fact that the physical as well as the chemical properties of the elements are periodic functions of the atomic weight.

This may be illustrated by reference to the magnetic properties of the elements. Faraday divided all substances into two classes: those which are attracted by a magnet, or *paramagnetic* bodies, and those which are repelled by a magnet or *diamagnetic* bodies. In the case of the elements, the magnetism of the following has been determined:

Paramagnetic Elements.

K, C, Ti, Ce, N, O, Cr, U, Mn, Fe, Co, Ni, Rh, Pd, Os, Ir, Pt.

Diamagnetic Elements.

H, Na, Cu, Ag, Au, Zn, Cd, Hg, Tl, Si, Sn, Pb, P, As, Sb, Bi, S, Se, Cl, Br, I.

An inspection of these two classes does not reveal any apparent connection between the chemical and the magnetic properties of the ele-

ments. Thus we find that elements, chemically so closely related as potassium and sodium, oxygen and sulphur, nitrogen and phosphorus, titanium and silicon, are separated in the two classes. Carnelley has, however, pointed out that the paramagnetic elements are, without exception, to be found in the *even series* of Mendeleef's table and the diamagnetic elements without exception in the *odd series*. Further, the paramagnetic power of the members of a paramagnetic group of elements (thus Fe, Co, Ni) diminishes, and the diamagnetic power of the members of a diamagnetic group of elements (thus P, Sb, Bi, or H, Cu, Ag, Au) increases, with increasing atomic weight.

The fact that the physical properties of the elements are a periodic function of their atomic weights is, however, most strikingly shown by the curve given in the annexed diagram. This curve, which is in reality a graphic expression of the periodic law, was first constructed by Lothar Meyer. It is given here as supplementing in a remarkable manner Mendeleef's table.

In this curve the abscissæ represent the atomic weights, and the ordinates the atomic volumes of the various elements in the solid state.* The curve is therefore primarily a graphic representation of the variation of the atomic volume with the atomic weight. But a brief inspection shows that it is much more than this.

In the first place then, as regards the atomic volume, the curve shows in the plainest manner that this varies periodically with the atomic weight: at one point it reaches a maximum, then gradually decreases with increasing atomic weight till it falls to a minimum, again rising to a maximum, and so on. Each of these compound periods of decrease and increase corresponds with one hollow of the wave of the curve extending from crest to crest. A comparison of this curve with Mendeleef's table is highly instructive, especially when we consider that the two were constructed quite independently of each other. In the curve the periods of change of atomic volume—the hollows—are distinguished by Roman numerals. Periods II. and III. of the curve correspond with Mendeleef's two "short periods," series 2 and 3 of the table. The large hollows of the curve, IV., V., etc., correspond with Mendeleef's "long periods:" thus Period IV. of the curve is the "long period" made up of series 4 and 5 of the table; Period V. is the "long period" made up of series 6 and 7 of the table, and so on. (The latter part of the curve has not been finished for want of data.) The alkali metals with which Mendeleef's periods commence are always found at the maxima of the curve. Mendeleef's "transitional elements" of Group VIII., the metals which lie between the even and odd series of a "long period," are always found at the minima of the large hollows. Osmium cannot, with its

* The atomic volumes of the elements are the relative volumes occupied by atomic quantities, *i.e.*, quantities taken in the proportion of the atomic weights. These atomic volumes may be found by dividing the atomic weights of the elements by their specific gravities (see following chapter). In the diagram, wherever the elements are not known in the solid state, the hypothetical course of the curve is represented by a dotted line. As regards the rather irregular course of the curve in some parts, it is to be noted that the specific gravities of the elements have not always been determined under strictly comparable conditions. Thus the specific gravity of potassium is determined a few degrees below its fusing-point; that of platinum about 2000° below the fusing-point.

present atomic weight, be made to fit into this curve, any more than into Mendeleef's table.

Various other periodic relations between the atomic weights and the physical properties of the elements have been indicated on the diagram by appending to each part of the curve a list of the physical properties of the elements to which that part refers. Thus, elements possessing the same physical properties are to be found in corresponding parts of the curve. It is to be noted, however, that the alternation of "electropositive—electronegative," which occurs only once in Period II. and only once in Period III. of the curve, occurs twice in Period IV. and twice in Period V. This is in harmony with the fact already referred to that Periods II. and III. correspond each with one series of Mendeleef's table; Periods IV. and V. each with two series.

It is quite inconceivable that the remarkable relationships expressed by the periodic law should be a work of chance.

No explanation of the periodic law has yet been offered. At present it is an empirical law, established by careful experiment and comparison. It stands in the same relation to chemistry as did the laws of Kepler to astronomy before the time of Newton. Its explanation will in all probability constitute the chemical theory of the future.

CHAPTER XI.

RELATIONS BETWEEN CHEMICAL COMPOSITION AND SPECIFIC GRAVITY. ATOMIC VOLUME.

THE relative volumes which atomic or molecular quantities (quantities taken in the proportion of the atomic or molecular weights) of substances occupy, may be found by dividing the atomic or molecular weights of these substances by their specific gravities. The quotients thus obtained are termed *atomic volumes* and *molecular volumes* respectively.

It must not be supposed that these quotients express the relative volumes occupied by the atoms or molecules. In the gaseous state the molecules are separated from each other by distances which are enormously great compared with the diameters of the molecules themselves. In the solid and liquid states, the atomic volumes could only represent the relative volumes of the atoms, provided that the spaces between the atoms were in every case proportional to the size of the atoms—an assumption for which there is not the slightest ground. The atomic volumes, therefore, represent the relative volumes of the atoms, *plus* the relative volumes of their interstitial spaces.

The molecular volumes of gases have already been treated of (p. 54), and may be dismissed in a few words. As the specific gravities or vapor-densities of gaseous bodies are proportional to their molecular weights, the quotient $\frac{\text{molecular weight}}{\text{vapor-density}}$ will in all

cases possess the same value. The value of this quotient is either 28.9 or 2, according as the vapor-density is referred to air or to hydrogen (see p. 53).

The laws which govern the relations between composition and specific gravity are less simple in the case of solids and liquids; but here also very striking regularities are manifested.

As the specific gravity of a solid or liquid denotes the weight in grams of one cubic centimetre of the substance, so the atomic or molecular volume, if the atomic or molecular weight be expressed in grams, will represent cubic centimetres. The atomic weight of sulphur is 32, its specific gravity 2. The atomic weight of lead is 206.5, its specific gravity 11.37. The atomic volume of sulphur is therefore 16, that of lead 18.2. In grams and cubic centimetres this may be expressed as follows: If 2 grams of sulphur occupy the volume of 1 c.c., 32 grams will occupy 16 c.c. If 11.37 grams of lead occupy the volume of 1 c.c., 206.5 grams will occupy 18.2 c.c.

Among the elements, the various members of an isomorphous group frequently exhibit approximate equality of atomic volume.

	Atomic weight.	Specific gravity.	Atomic volume.
Iron, ...	56	7.79	7.2
Cobalt, ...	58.6	8.60	6.8
Copper, ...	63.2	8.95	7.1
Manganese, ...	55	8.00	6.9
Nickel, ...	58.6	8.90	6.6

Again:

Iridium, ...	192.5	22.38	8.6
Palladium, ...	105.7	11.40	9.2
Platinum, ...	194.4	21.53	9.0
Rhodium, ...	104	12.10	8.6

The members of an isomorphous group of compounds generally have approximately the same equivalent volume. In the group of the spinelles, which crystallize in forms of the regular system, these relations are as follows:

	Molecular weight.	Specific gravity.	Molecular volume.
MgO,Al_2O_3, ...	142.4	3.45	41.3
ZnO,Al_2O_3, ...	183.3	4.58	40.0
MnO,Cr_2O_3, ...	224	4.87	46.0
ZnO,Cr_2O_3, ...	233.3	5.31	43.9
ZnO,Fe_2O_3, ...	241.3	5.13	47.0
FeO,Fe_2O_3, ...	232	5.09	45.6

The subject of atomic and equivalent volumes of solids has been investigated by H. Kopp, Schröder, and others.

The molecular volumes of liquids, when compared at the same temperature, display no regularities. If, however, these volumes be determined at temperatures at which the tensions of the vapors of the liquids are equal, that is to say, at temperatures at which the energy of the molecules which fly off from the surface of each liquid is equal, and at which temperatures consequently the liquids are in the same condition as regards the weakening of the force of cohesion, important laws become manifest. Under such conditions, it seems that each element has one or more fixed atomic volumes, and that the molecular volume of a compound in the liquid state is the sum of the atomic volumes of its elements. As the vapor-tensions of most liquids have not been determined for a variety of temperatures, it is usual to compare the molecular volumes at the boiling-points of the liquids, at which temperatures the tensions of their vapors are equal to the normal atmospheric pressure (see p. 120).

These laws may be deduced and expressed as follows:

1. A difference of $n.CH_2$ in the formula of liquid compounds corresponds to a difference of n.22 in the molecular volume. Thus, methylic formate ($C_2H_4O_2$), methylic acetate ($C_3H_6O_2$), ethylic acetate ($C_4H_8O_2$), and methylic butyrate ($C_5H_{10}O_2$), whose formulæ differ by CH_2, differ in molecular volume by nearly 22. (For a comparison of the experimental with the calculated results, see table, p. 101.)

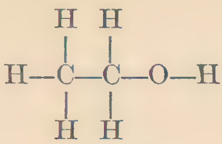
2. Isomeric liquids, belonging to the same chemical type, such as acids and ethereal salts, alcohols and ethers, ketones and aldehydes, have the same molecular volume. Thus, the molecular volumes of propionic acid, ethylic formate and methylic acetate, all of which have the formula $C_3H_6O_4$, closely approximate to 86.

3. The substitution of one atom of oxygen for two of hydrogen causes a slight increase of molecular volume. The molecular volume of alcohol (C_2H_6O) is between 61.8 and 62.5, that of acetic acid ($C_2H_4O_2$) lies between 63.5 and 63.8. Cymene ($C_{10}H_{14}$) and cuminaldehyde ($C_{10}H_{12}O$) differ similarly in their molecular volumes.

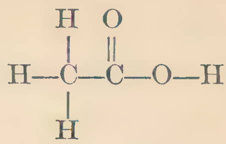
4. In two liquids belonging to the same chemical type, the substitution of one atom of carbon for two atoms of hydrogen produces no change of molecular volume. This may be seen in the case of ethylic benzoate ($C_9H_{10}O_2$) and ethylic valerate ($C_7H_{14}O_2$); benzaldehyde (C_7H_6O) and valeraldehyde ($C_5H_{10}O$); cymene ($C_{10}H_{14}$) and butyl (C_8H_{18}).

As the addition of CH_2 to the formula of a compound produces an increase of 22 in the equivalent volume (Law 1), this number may be supposed to represent the equivalent volume of CH_2. And since (Law 4) the exchange of C for H_2 causes no change of molecular volume, the atomic volume of C may be taken to be equal to that of H_2. Hence, the atomic volume of C is equal to $\frac{22}{2} = 11$, and that of H_2 is also equal to 11, or that of $H = 5.5$. From the increase in molecular volume which the substitution of O for H_2 causes, the atomic volume of O may be calculated to be equal to 12.2. In this case when O is substituted

for H_2, both its bonds are attached to the same atom of carbon, as for example when alcohol is converted into acetic acid.



Alcohol.



Acetic acid.

It will be convenient, in discussing the subject of atomic volumes, to represent oxygen thus attached by the ordinary symbol O, whereas oxygen which serves to unite two elements or groups of elements, as in the case of hydroxylic oxygen, or of oxygen in ethylic oxide, will be distinguished by the symbol Ⓞ. It is found that the atomic volume of Ⓞ is different from that of O. The value of the former may be deduced from the molecular volume of water.

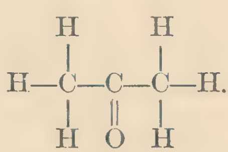
Molecular volume of		ⓄH_2	=	18.8
Atomic	"	H_2	=	11
"	"	Ⓞ		7.8

From these four atomic volumes,

Atomic volume of		C	=	11
"	"	H	=	5.5
"	"	O	=	12.2
"	"	Ⓞ	=	7.8

the molecular volumes of compounds containing only these four elements may be calculated. The numbers so deduced approximate very closely to those obtained by experiment. It is evident that the value to be assigned to the atomic volume of oxygen will depend upon the constitution of the compound, and that, conversely, the molecular volume of a compound containing oxygen will afford a means of ascertaining the part which this element plays in its constitution. A few examples will suffice.

The graphic formula of acetone is



From this formula follows:

Atomic volume of		C_3	=	33
"	"	H_6	=	33
"	"	O	=	12.2
Molecular volume of acetone			=	78.2

The molecular volume of acetone as determined by experiment is between 77.3 and 77.6.

The graphic formula of alcohol has been given on p. 99. The molecular volume would be calculated thus:

Atomic volume of	C_2	=	22
" "	H_6	=	33
" "	$\ominus$	=	7.8
Molecular volume of alcohol		=	62.8

The observed volume is between 61.8 and 62.5.

The graphic formula of acetic acid has been given on p. 99. Its molecular volume would be as follows:

Atomic volume of	C_2	=	22
" "	H_4	=	22
" "	O	=	12.2
" "	$\ominus$	=	7.8
Molecular volume of acetic acid		=	64.0

The experimental value is between 63.5 and 63.8.

The subject of the molecular volumes of liquids has been investigated chiefly by H. Kopp, to whom the enunciation of the above laws is due.* The following table contains a list of his determinations of molecular volumes at the boiling-point for a number of liquids into the composition of which only carbon, hydrogen, and oxygen enter. The third column contains the temperatures at which the determinations were made.

* Recently the subject has been studied by Thorpe, Ramsay, and others.

Molecular Volumes of Liquids containing Carbon, Hydrogen, and Oxygen.

Substance.	Formula.	Temperature.		Molecular volume.	
				Observed.	Calculated.
Benzene, ...	C_6H_6	80° C.	176° F.	96 0— 99.7	99.0
Cymene, ...	$C_{10}H_{14}$	175	347	183.5—185.2	187.0
Naphthalene, . .	$C_{10}H_8$	218	424	149.2	154.0
Aldehyde, . . .	C_2H_4O	21	70	56.0— 56.9	56.2
Valeraldehyde, . .	$C_5H_{10}O$	101	114	117.3—120.3	122 2
Benzaldehyde, . .	C_7H_6O	179	354	118.4	122.2
Cuminaldehyde, .	$C_{10}H_{12}O$	236	457	189.2	188.2
Butyl, ...	C_8H_{18}	108	226	184.5—186.6	187.0
Acetone, ...	C_3H_6O	56	133	77.3— 77.6	78.2
Water, ...	ΘH_2	100	212	18.8	18.8
Methylic alcohol, .	$CH_4\Theta$	59	138	41.9— 42.2	40.8
Ethylic " .	$C_2H_6\Theta$	78	172	61.8— 62.5	62.8
Amylic " .	$C_5H_{12}\Theta$	135	275	123.6—124.4	128.8
Phenol, ...	$C_6H_6\Theta$	194	381	103.6—104.0	106.8
Benzylic alcohol, .	$C_7H_8\Theta$	213	415	123.7	128.8
Formic acid, . .	$CH_2O\Theta$	99	210	40.9— 41.8	42.0
Acetic " . .	$C_2H_4O\Theta$	118	244	63.5— 63.8	64.0
Propionic " . .	$C_3H_6O\Theta$	137	279	85.4	86.0
Butyric " . .	$C_4H_8O\Theta$	156	313	106.4—107.8	108.0
Valeric " . .	$C_5H_{10}O\Theta$	175	347	130.2—131.2	130.0
Benzoic " . .	$C_7H_6O\Theta$	253	487	126.9	130.0
Ethylic oxide, . .	$C_4H_{10}\Theta$	34	93	105.6—106.4	106.8
Acetic anhydride, .	$C_4H_6O_2\Theta$	138	280	109.9—110.1	109.2
Methylic formate, .	$C_2H_4O\Theta$	36	97	63.4	64.0
Methylic acetate, .	$C_3H_6O\Theta$	55	131	83.7— 85.8	86.0
Ethylic formate, .	$C_3H_6O\Theta$	55	131	84.9— 85.7	86.0
Ethylic acetate, .	$C_4H_8O\Theta$	74	165	107.4—107.8	108 0
Methylic butyrate, .	$C_5H_{10}O\Theta$	93	199	125.7—127.3	130.0
Ethylic propionate,	$C_5H_{10}O\Theta$	93	199	125 8	130.0
Methylic valerate, .	$C_6H_{12}O\Theta$	112	234	148.7—149 6	152.0
Ethylic butyrate, .	$C_6H_{12}O\Theta$	112	234	149.1—149.4	152.0
Butylic acetate, . .	$C_6H_{12}O\Theta$	112	234	149.3	152.0
Amylic formate, .	$C_6H_{12}O\Theta$	112	234	149.4—150 2	152.0
Ethylic valerate, .	$C_7H_{14}O\Theta$	131	268	173.5—173.6	174.0
Amylic acetate, . .	$C_7H_{14}O\Theta$	131	268	173.3—175.5	174.0
Amylic valerate, .	$C_{10}H_{20}O\Theta$	188	370	244.1	240.0
Methylic benzoate,	$C_8H_8O\Theta$	190	374	148.5—150.3	152 0
Ethylic "	$C_9H_{10}O\Theta$	209	408	172.4—174.8	174 0
Amylic "	$C_{12}H_{16}O\Theta$	266	511	247.7	240.0
Ethylic cinnamate,	$C_{11}H_{12}O\Theta$	260	500	211.3	207.0
Methylic salicylate,	$C_8H_8O\Theta_2$	223	433	156.2—157.0	159.8
Ethylic carbonate,	$C_5H_{10}O\Theta_2$	126	259	138.8—139.4	137.8
Methylic oxalate, .	$C_4H_6O_2\Theta_2$	162	324	116.3	117.0
Ethylic " .	$C_6H_{10}O_2\Theta_2$	186	367	166.8—167.1	161.0
Ethylic succinate, .	$C_8H_{14}O_2\Theta_2$	217	423	209.0	205.0

In like manner, from the molecular volumes of the liquid chlorides, bromides, and iodides, the atomic volume of Cl has been determined to be equal to 22.8, that of Br = 27.8, and that of I = 37.5.

Elements of varying atomicity like nitrogen and sulphur seem to follow some less simple law. It is possible that the atomic volumes of these elements may vary in some way with their atomicity; but the precise nature of this variation has not been ascertained. The subject requires thorough investigation by the light of modern constitutional formulæ.

CHAPTER XII.

CHEMICAL AFFINITY.

CHEMICAL affinity has been referred to at some length in the opening pages of this introduction. It may be measured as regards its *extent* and as regards its *intensity*. A measure of the *relative extent of the chemical affinity* of two or more elements for some other element is afforded by the number of atoms of this element with which each can combine. *Extent of affinity* is thus directly connected with *atomicity*. *Relative intensity of affinity* of two or more elements for any given element refers to the resistance which their compounds with this element offer to decomposition. The measure of this intensity is the quantity of heat evolved in combination or required for decomposition.

Extent and intensity of affinity are quite independent of each other. Thus copper and mercury in the compounds CuO and HgO have the same extent of affinity for oxygen; but since mercuric oxide breaks up at a relatively low temperature into its constituents, whereas cupric oxide does not undergo decomposition until a temperature above 1000° C. has been reached, and then yields up only a portion of its oxygen, the intensity of affinity for oxygen is much greater in the case of copper. Again, the extent of affinity of carbon towards hydrogen is four times as great as that of chlorine. This may be seen in methylic hydride (CH_4) and hydrochloric acid (HCl). But whereas carbon and hydrogen cannot be made to combine directly at all, chlorine and hydrogen unite with evolution of great heat. Here the element of greatest extent of affinity has least intensity of affinity. One atom of phosphorus can unite with three atoms of chlorine, giving off much heat, and forming a compound which may be distilled without decomposition; one atom of silver can unite with only one atom of chlorine, and the resulting compound is decomposed by the action of daylight. Here extent and intensity of affinity go together.*

MODES OF CHEMICAL ACTION.—Matter undergoes chemical change in five different ways, viz.:

1st. By the direct combination of elements or compounds with each other.

2d. By the displacement of one element or group of elements in a body by another element or group of elements.

* The above can be regarded only as an approximately correct statement. In nearly every so-called direct combination of elements there is a preliminary decomposition of elementary molecules:

$$H_2 + Cl_2 = 2HCl.$$

Here the affinity of hydrogen for chlorine is the force which strives to bring about the reaction, and in this it is opposed by the two affinities of hydrogen for hydrogen, and of chlorine for chlorine, which have to be overcome before the reaction can occur. Thus, the apparently lower affinity of carbon for hydrogen may in reality consist in a higher affinity of carbon for carbon—the affinity of hydrogen for hydrogen remaining, of course, the same in both reactions.

For the same reason the heat of combination is a complex quantity, and cannot be regarded as an *infallible* measure of the intensity of affinity (see Thermochemistry).

3d. By a mutual exchange of elements or groups of elements in two or more bodies.

4th. By the rearrangement of the elements or groups of elements already contained in a body.

5th. By the resolution of a compound into its elements, or into two or more less complex compounds.

Illustrations of these five modes of chemical action have already been given (p. 76).

COMBINATION.—The part of this subject which refers to the fixed proportions in which the elements combine, has been fully treated of under *Laws of Combination* (Chap. IV.). But not only are the proportions by weight in which every combination takes place perfectly definite, but the amount of heat liberated or absorbed in each combination is also a fixed quantity (see *Heat of Chemical Combination*, Chap. XV.).

DECOMPOSITION.—The forces which accomplish the resolution of a compound, either into simpler compounds, or into its elements, have been referred to on pp. 36 and 49. The chief of these forces are heat and electricity. The action of heat has frequently been described in the course of this introduction.

In the decomposition of compounds by heat two cases may be distinguished, according as the products of decomposition have, or have not, a tendency to re-combine and form the original compound. Decomposition in which this regenerative tendency exists is known as *dissociation*. The phenomena of dissociation have been very carefully studied, and, in regard to these, definite laws have been deduced; whereas in the case of the more complex phenomena of ordinary decomposition by heat general principles have yet to be discovered.

Decomposition by means of the electric current is termed *electrolysis*, and the compound which is thus decomposed is termed an *electrolyte*. The electrolyte must be in the liquid condition—either in solution or in a state of fusion. The current from a voltaic battery, when passed through the electrolyte, decomposes it into two constituents known as *ions*. The terminals of the battery, which are immersed in the electrolyte and on the surfaces of which the separation of the ions occurs, are termed *electrodes*. The material of the electrodes may vary according to circumstances, but plates of platinum are generally employed in the case of solutions.

Dissociation.—Examples of dissociation have already been given (see *Apparent Exceptions to Avogadro's Law*, p. 63). Further examples of dissociable compounds are—the aquates of some salts, which by heating give off their water of crystallization; and the carbonates, most of which at a sufficiently elevated temperature evolve carbonic anhydride. A very important law of dissociation is, that the volatile products given off by a substance undergoing dissociation have a *constant tension for each temperature*. This tension corresponds exactly in character to the tension of the vapor of a liquid, and its amount may be measured in the same way (see Chap. XVII.). The tension of dissociation depends entirely on the temperature, being higher for higher temperatures; and is quite independent both of the space filled by the volatile products

and of the quantity of substance which has already undergone decomposition. Thus Debray (*Compt. Rend.*, 64, 603) has shown that the tension of dissociation of calcic carbonate is not altered by the addition of an excess of quicklime—the solid product of decomposition.

Decomposition may also be effected by means of the electric spark, which may be applied either in the form of the voltaic arc or as the induction spark. In both cases the electric discharge acts *solely by its heating effect*, and its action must therefore not be confounded with electrolysis. It differs from other sources of heat in being at the same time local and more intense. If a series of induction sparks be passed through carbonic anhydride, those molecules which lie in the path of the spark are broken up by the heat into carbonic oxide and oxygen. The moment the molecules of the two latter gases pass beyond the immediate sphere of the spark, they reach a relatively cold region, the temperature of which lies far below their temperature of combination, so that they can continue to exist in the free state.

If, in the above experiment, the proportion of decomposed carbonic anhydride be allowed to pass beyond a certain limit, re-combination of the oxygen and carbonic oxide will take place with explosion. This occurs as soon as a sufficient number of molecules of the two latter gases are present to propagate the heat of combination through the body of the gas. This propagation is impossible as long as their molecules are separated by a large number of indifferent molecules of carbonic anhydride.

Electrolysis.—The following are the laws of electrolysis:

1. The liquid condition is necessary to electrolysis.

2. Electrolytes must be compounds and conductors of the electric current. These compounds generally consist of a conductor and a non-conductor of electricity.

3. Compounds which suffer electrolysis when dissolved in water do so also when fused.

4. The electrolyte is resolved into two constituents, which, impelled in opposite directions, are eliminated at the opposing surfaces of the two electrodes, and never in the intervening liquid.

5. Oxygen, chlorine, bromine, iodine, and acids appear at the positive electrode, and are, therefore, electro-negative; whilst hydrogen, metals, and alkalies are evolved at the negative electrode, and are, therefore, electro-positive.

6. The quantity of electricity which passes through the electrolyte is always directly proportional to the quantity of the electrolyte which is decomposed.

7. All compound molecules possessing the same active atomicity to be overcome, require, if decomposable, the same quantity of electricity to decompose them. Therefore, if the same electric current be passed through a number of metallic solutions in succession, the metals will be reduced in the ratio of their atomic weights divided by their active atomicities.

8. The quantity of electricity which a compound molecule requires to decompose it, is equal to the quantity which that molecule evolves when it is formed in the generating cell of the battery.

9. The quantity of electricity evolved by the union of two or more bonds, is capable of effecting the disruption of the same number of bonds in any compound susceptible of electrolysis.

The following is a list of weights of various chemical compounds requiring for their decomposition equal quantities of electricity:

Water, ...	$\frac{1}{2}(O''H_2)$	9.0 grams.
Hydrochloric acid, ...	HCl	36.5 "
Argentic chloride, ...	$AgCl$	143.2 "
Cupric chloride, ...	$\frac{1}{2}(Cu''Cl_2)$	67.1 "
Cuprous chloride, ...	$\frac{1}{2}('Cu'_2Cl_2)$	98.7 "
Plumbic chloride, ...	$\frac{1}{2}(Pb''Cl_2)$	138.7 "
Antimonious chloride, . . .	$\frac{1}{3}(Sb'''Cl_3)$	75.5 "
Plumbic iodide, ...	$\frac{1}{2}(Pb''I_2)$	230.2 "
Plumbic acetate, ...	$\frac{1}{2}(Pb''\overline{A}c_2)$	162.2 "
Cupric sulphate, ...	$\frac{1}{2}(SO_4Cu'')$	79.6 "
Zincic sulphate, ...	$\frac{1}{2}(SO_4Zn'')$	80.6 "
Stannous chloride, ...	$\frac{1}{2}(Sn''Cl_2)$	94.5 "
Ferrous chloride, ...	$\frac{1}{2}(Fe''Cl_2)$	63.5 "
Ferric chloride, ...	$\frac{1}{6}('Fe'''_2Cl_6)$	54.2 "

Thus if the electric current were passed through argentic chloride, cupric chloride, and cuprous chloride, included in the same circuit; by the time 143.2 grams of argentic chloride had been decomposed, the quantities of cupric and cuprous chlorides which had undergone decomposition would be 67.1 grams and 98.7 grams respectively. The weight of silver deposited from the first salt would be 107.7 grams; that of copper from the other two 31.6 grams and 63.2 grams, the quantity being in every case in the proportion of the atomic weight of the metal, divided by its active atomicity.

What is termed *secondary action* in electrolysis takes place when the primary products of decomposition exert a chemical action, either on the solvent, or on other substances which are present, or on the electrolyte itself. Thus when a solution of sodic chloride is electrolyzed, the salt is broken up into sodium and chlorine. The sodium, however, does not make its appearance as such, but decomposes the water with evolution of hydrogen and formation of sodic hydrate:

$$\underset{}{Na_2} + \underset{\text{Water.}}{2OH_2} = H_2 + \underset{\text{Sodic hydrate.}}{2ONaH.}$$

Hydrogen and chlorine are thus obtained in the electrolysis of a solution of sodic chloride, but the hydrogen is a secondary product. Again, if a mixed solution of hydrochloric and hydriodic acids is electrolyzed, no chlorine is evolved, since chlorine instantaneously liberates iodine from the hydriodic acid, regenerating hydrochloric acid. Again, if the positive electrode consists of an oxidizable metal, the electronegative element or group will combine with it. Thus, if acidulated water be electrolyzed with copper as the positive electrode the copper will go into solution, and form a copper salt with the acid.

The electrolysis of sulphuric acid and plumbic sulphate has of late

acquired great importance in connection with secondary batteries or accumulators as an economic means of storing energy. Various forms of storage battery have been suggested, but all are modifications of the original invention of Planté. They consist essentially of plates composed of or coated with plumbic sulphate, these plates being arranged as in primary batteries and immersed in dilute sulphuric acid.

When an electric current, either from a primary battery or a dynamo-electric machine, is passed through the cells of a secondary battery, employing the plates of plumbic sulphate as electrodes, the intervening hexabasic sulphuric acid is electrolyzed according to the following equation:

$$\mathbf{SHo_6} = \underbrace{\mathbf{SO_3} + 3\mathrm{O}}_{\text{On + plate.}} + \underbrace{3\mathrm{H_2}}_{\text{On — plate.}}$$

The sulphuric anhydride thus liberated is immediately reconverted into hexabasic sulphuric acid:

$$\mathbf{SO_3} + 3\mathbf{OH_2} = \mathbf{SHo_6}.$$

The nascent oxygen in contact with the plumbic sulphate on the positive plate converts the lead salt into plumbic peroxide ($\mathbf{PbO_2}$), liberating sulphuric anhydride, which in contact with water regenerates hexabasic sulphuric acid as just described.

The nascent hydrogen on the negative plate converts the plumbic sulphate into lead and hexabasic sulphuric acid:

$$\underset{\text{Plumbic sulphate.}}{\mathrm{SO_2Pbo''}} + \mathrm{H_2} + 2\mathbf{OH_2} = \mathrm{Pb} + \underset{\text{Hexabasic sulphuric acid.}}{\mathbf{SHo_6}}.$$

Under the influence of an electric current, therefore, the opposing plates of the secondary battery become coated, the one with plumbic peroxide, and the other with metallic lead, the latter being in a spongy state; and they are in a highly electro-polar condition. On joining them by a conductor, a powerful electric current, with an electromotive force of about 2.4 volts for each cell, flows through the conductor from the plate coated with peroxide of lead to that coated with spongy lead, whilst within the cell the current passes through the dilute sulphuric acid in the opposite direction, viz., from lead to peroxide of lead, decomposing the acid as in charging. As, however, the current now flows in a direction opposite to that during charging, the ions are liberated on the opposite plates. On the positive plate, which was formerly the negative electrode, the chemical change is as follows:

$$\underset{\text{Plumbic peroxide.}}{\mathbf{PbO_2}} + \mathrm{H_2} = \underset{\text{Plumbic oxide.}}{\mathbf{PbO}} + \mathbf{OH_2}.$$

The plumbic oxide, which is thus formed in contact with sulphuric acid, is converted into plumbic sulphate.

On the negative plate, which was the positive electrode, the following action takes place:

$$Pb + O + \underset{\text{Hexabasic sulphuric acid.}}{SHo_6} = \underset{\text{Plumbic sulphate.}}{SO_2Pbo''} + 3OH_2.$$

During the discharge, therefore, both plates return to their original condition.

Instead of discharging the plates immediately, however, the energy invested in them may, with but inconsiderable loss, be allowed to remain stored for weeks, or even months, ready at any moment to yield a powerful electric current available for the production of light, heat, or mechanical power.

Electrochemical Equivalents.—For some time after the revival of the atomic theory in its chemical form by Dalton, chemists were at a loss which of several possible atomic weights of an element to accept as the true one. The laws of vapor-density, of specific heat, of isomorphism, were enunciated not very long after; but as their significance was not generally perceived, their application as a means of checking the atomic weights was out of the question. In the midst of the uncertainty which prevailed, the law of electrolysis as stated by Faraday was eagerly welcomed. According to this law the quantities of various electrolytes decomposable by the same current are chemically equivalent, and the quantities of the several elements eliminated in such decompositions are also chemically equivalent. On this principle chemists constructed tables of *equivalents* of the elements, representing the relative weights which are eliminated in electrolysis, that of hydrogen being taken as unity. Such equivalents would be, for example:

$$\begin{aligned} H &= 1 \\ O &= 8 \\ Cl &= 35.5 \\ S &= 16 \\ Pb &= 103.25 \end{aligned}$$

etc.

This mode of procedure was thus far strictly legitimate, inasmuch as the above weights can replace each other in chemical combination, and are therefore equivalent. But most chemists went further than this, and assumed that these equivalents were identical with the atomic weights of the elements. By this means the significance of the above-mentioned three important laws was effectually obscured, and a true chemical classification was for many years rendered impossible.

Furthermore, the system of equivalents was not logically carried out. The electrolytic equivalent of antimony is 40; but instead of this the number 120, its present atomic weight, was adopted. The same happened with several other elements.

Another objection to this system is that the equivalent of an element does not, like its atomic weight, represent a constant quantity, but varies with the active atomicity. This may be seen in the case of copper in its cuprous and cupric salts.

A knowledge of the so-called equivalent notation is necessary for the study of many important works on chemistry in which it is employed.

The old equivalent formulæ may be converted into modern atomic formulæ, either by doubling the number of the perissad, or by halving that of the artiad atoms (see p. 79). Thus:

	Old so-called equivalent formula.	Atomic formula.
Water, ...	HO	H_2O
Sulphuric acid, ...	HSO_4	H_2SO_4
Nitric acid, ...	HNO_6	HNO_3
Ferric chloride, ...	Fe_2Cl_3	Fe_2Cl_6

In modern works equivalent formulæ, when quoted, are generally written as above, in italics.

The fact that a single atom of one element may be equivalent to two or more atoms of another, sufficiently explains the discrepancies between atomic and equivalent proportions noticed in treating of the law of equivalent proportions (see p. 47).

CHAPTER XIII.

CHEMICAL HOMOGENEITY.

A CHEMICALLY homogeneous substance is one in which all the molecules are exactly alike. It is evident from this definition that such a substance will exhibit constant composition: if it is a simple body, it will yield on analysis no other body; if it is a compound, it will contain the same ingredients in unvarying proportion. But in the case of compounds, analysis alone cannot furnish complete evidence of the homogeneous nature of a substance: for example, it is plain that a mixture of molecular proportions of manganous oxide (**MnO**) and manganic peroxide (**MnO_2**), would yield analytical results corresponding to manganic oxide (**Mn_2O_3**). Hence, other means of identification are necessary, and these are frequently to be found in the physical properties of the substance.

Thus, all substances, in whatever physical state they exist—gaseous, liquid, or solid—possess a definite specific gravity at a given temperature. The specific gravities of the more important chemically homogeneous substances have been determined, and it is thus frequently possible to identify a substance, as it is not probable that a mixture accidentally possessing a percentage composition the same as that of a true chemical compound, would also have the same specific gravity. This characteristic is least certain in the case of solids, where a slight alteration in physical condition, such as that produced in metals by hammering, is sufficient to cause a change in the specific gravity. Such variations, however, occur within narrow limits.

The number of the characteristics available for establishing the chemical homogeneity of substances varies with the complexity of the phys-

ical state, being greatest in the case of solids, and smallest in the case of liquids.

Gases.—A mixture of equal volumes of methylic hydride (CH_4) and propylic hydride (C_3H_8) would yield not only the same analytical results as ethylic hydride (C_2H_6), but would also possess the same specific gravity. In this case the best method of determining whether the gas is single or a mixture, is to submit it to diffusion. For this purpose, it is transferred to a tube over mercury, closed at the upper extremity by a porous diaphragm (graphite or gypsum). By the law of diffusion (*q.v.*) the lighter molecules will pass through the diaphragm more rapidly than the heavier molecules. If, therefore, in the above case, on examining the residual gas, the proportions of carbon and hydrogen be found to have changed, it may be concluded that the original gas was a mixture; if these proportions remain the same, then either the gas is single or it is a mixture in which each gas is present in the ratio of its coefficient of diffusion, a case which must necessarily be of very rare occurrence. Sometimes the gas is submitted to the action of various absorbents—caustic potash, potassic pyrogallate, fuming sulphuric acid. If part be absorbed by any of these reagents, whilst part remains unacted upon, it is at once proved that the gas is a mixture.

Liquids.—When a liquid can be distilled without decomposition, its boiling-point affords one of the best tests of its homogeneity. Every chemical compound which is capable of volatilizing without decomposition, has, at a given barometric pressure, a fixed boiling-point, at which it must distil from the first to the last drop. As a rule, a mixture of two liquids of different boiling-points will begin to boil about the boiling-point of the lowest, and a thermometer placed in the vapor will in turn indicate all temperatures up to the boiling-point of the highest. Mixed liquids may be separated by *fractional distillation;* the fractions of the distillate passing over at different temperatures are collected separately, and these fractions are redistilled until liquids of constant boiling-point are obtained. Some liquids cause the plane of a ray of polarized light which passes through them to rotate to the right or to the left, and, as this rotation is constant for a given stratum of a given liquid, the action on polarized light may be frequently employed in the case of such liquids as a test of their purity.

Solids.—When a solid possesses the property of crystallizing, its crystalline form offers the surest means of identifying it. If the crystals are so well developed that their angles may be measured, the values of these angles, coupled with the analytical results, suffice to place the identity of any substance for which such determinations have previously been made, beyond all possibility of doubt. Even when the crystals are too small to admit of measurement, a microscopic examination will generally be sufficient to decide whether they are homogeneous or mixed. Heterogeneity of crystalline form does not *necessarily* involve chemical difference; a substance may be dimorphous. Thus the sublimate of arsenious anhydride frequently contains, side by side, rhombic prisms and regular octahedra. When solids are fusible, they possess a constant fusing-point. This property is of great value in identifying organic substances, of which the greater number fuse within the limits

of the mercurial thermometer. As mixtures fuse at a lower temperature than the mean fusing-point of their constituents, impurities generally tend to lower the fusing-point. Every soluble solid, when pure, has a fixed solubility for each of its solvents at a given temperature. This solubility generally increases with the temperature (see Solubility). If the various ingredients of a mixture possess very different solubilities, this property may be taken advantage of in order to effect their separation, as the least soluble will crystallize out first, and, by repeated recrystallization, may generally be obtained pure. What is known as *fractional crystallization* consists in evaporating the solution of a substance until sufficiently concentrated to crystallize. The liquid is then separated from the crystals and evaporated until a fresh crop of crystals is obtained. This process is repeated until the solution is exhausted. If the last crop of crystals is exactly like the first, as regards composition, form, fusing-point, etc., it may be concluded that the substance was homogeneous. The reverse of fractional crystallization is *fractional solution*. The solid substance is successively extracted with small portions of the solvent. In this way the more soluble ingredients, if such are present, will be removed. Sometimes various solvents are employed in succession, according to the nature of the substances suspected to be present in a mixture; and in this way a separation may frequently be effected. *Fractional precipitation* consists in adding to a solution a precipitant in quantity insufficient to precipitate the whole of the substance present. In a mixture, the various ingredients will probably be affected in varying degrees by the precipitant—that, for example, which has the greatest affinity for the precipitant will be found chiefly in the first fraction. By redissolving this fraction and partially precipitating it, and repeating this operation each time with the partial precipitates, one of the ingredients of the mixture may usually be obtained pure. This process is seldom necessary in the case of inorganic compounds, as with these a sharp separation by means of precipitants is generally at once possible. *Fractional saturation* is analogous to fractional precipitation, and depends on the varying degrees of affinity which the ingredients of a mixture exhibit towards the saturant. A mixture of bases, for example, is imperfectly saturated with an acid; a mixture of acids, with a base.

These fractional methods are chiefly of use in the case of organic compounds, which very seldom possess properties such as to render them separable from each other by a single operation. In the case of single substances such methods afford a guarantee of purity by the correspondence of the different fractions; and, in the case of mixtures, they yield, by systematic repetition, a means of separating the various ingredients.

CHAPTER XIV.

ISOMERISM, METAMERISM, POLYMERISM, ALLOTROPY.

COMPOUNDS which, while possessing the same percentage composition, exhibit differences of chemical and physical character, are termed *isomeric*. *Metamerism* and *polymerism* are special cases of isomerism;

metameric compounds have the same molecular weight, the difference in properties depending on difference of arrangement of the atoms within the molecule; in polymeric compounds the molecular weights are different, one being a multiple of the other. Examples of metamerism and polymerism are most common among the compounds of carbon, where the frequency of high molecular weights and the property which carbon possesses of repeatedly combining with itself, favor variety of atomic arrangement. The compounds propionaldehyde, acetone, allylic alcohol, propylenic oxide, and trimethylenic oxide, all possess the molecular formula C_3H_6O, and are, therefore, metameric. The hydrocarbons of the ethylenic or C_nH_{2n} series, ethylene (C_2H_4), propylene (C_3H_6), butylene (C_4H_8), etc., are polymeric. The single members of this group may possess metamers; thus, there are three butylenes of the formula C_4H_8—butylene, isobutylene, and pseudobutylene.

Allotropy stands in the same relation to elements that isomerism does to compounds. Many of the elements exist in several different modifications, possessing entirely distinct properties. Carbon is known in three forms: as charcoal, as graphite, and as diamond. Sulphur and phosphorus also possess allotropic modifications. One of the most striking and instructive instances of this phenomenon is found in the case of oxygen in its two modifications of common oxygen and ozone.

It is probable that allotropy is to be explained by reference rather to polymerism than to metamerism. It is certainly conceivable that molecules containing equal numbers of only one kind of atom should differ through the arrangement of these atoms within the molecule; but a difference of properties can more easily be accounted for by supposing that the molecules of the allotropic modification contain different numbers of atoms, and in the only case of true allotropy in which the molecular weights of the allotropic modifications are known, this is found to be the case. Common oxygen contains two atoms in the molecule, whereas ozone contains three.

It is to be noted that allotropy has been observed only in the case of polyad elements. The atoms of a monad element can only combine with each other in pairs, thus H—H, and in this way all variety, either in the number of atoms in the molecule, or in their arrangement, is excluded.

CHAPTER XV.

HEAT OF CHEMICAL COMBINATION. THERMOCHEMISTRY.

THERMOCHEMISTRY, that branch of the science which deals with the heat liberated or absorbed in chemical action, has been studied in great detail by Berthelot, Thomsen, and others. The first-named chemist has published (*Ann. Chim. Phys.* [4], VI., and [5], IV.) a summary of the results obtained in this field, and from this source the annexed account is extracted. He enunciates as the three fundamental laws of thermochemistry the following:

1. *Law of Molecular Work.*—The quantity of heat liberated in any reaction is a measure of the sum of the chemical and physical work performed in that reaction.

2. *Law of the Equivalence of Heat and Chemical Change.*—When a system of bodies, simple or compound, taken in definite conditions, undergoes physical or chemical changes which are capable of bringing the system into a new state without producing any mechanical effect external to the system, the quantity of heat liberated or absorbed during these changes depends solely on the initial and final states of the system, and remains the same, whatever be the nature and order of the intermediate states.

3. *Law of Maximum Work.*—Every chemical change, accomplished without the intervention of foreign energy, tends to the production of that body, or system of bodies, in the formation of which most heat is liberated.*

The first two laws are corollaries of the law of the conservation of energy; the third must be developed more in detail. It is possible to conceive the necessity of this law by considering that the system which has given off most heat no longer possesses the energy necessary to accomplish a fresh transformation. Every fresh change involves the performance of work, and this work cannot be performed without the intervention of foreign energy. On the other hand, a system capable of liberating heat by a fresh change, still possesses the energy requisite to produce this change without foreign aid. It is in the same way that a system of heavy bodies tends to that arrangement of its parts in which the centre of gravity is as low as possible; but the system will only attain to this arrangement should no foreign obstacle intervene. This is, however, rather an illustration than a demonstration.

In the equations which will now be employed in proof of this law, the atomic and molecular weights are to be understood in grams. The units of heat will then be calories (see p. 68). The latter are written to the right of the equation, and denote the heat liberated by the combination represented in the equation, supposing the combining quantities to be taken, as stated above, in the proportion of grams.

Combination.—According to the law of maximum work, oxygen, in combining with other bodies, will form a higher oxide or a lower oxide, according as the one or the other stage corresponds to the greater liberation of heat.

In the formation of nitrous anhydride from two molecules of nitric oxide and one atom of oxygen, the thermal effect is as follows:

$$\underset{\text{Nitric oxide.}}{2'\mathbf{N}''O} + O = \underset{\text{Nitrous anhydride.}}{\mathbf{N}_2O_3}, \quad . \; . \; . \; . \quad 20{,}000 \text{ cal.}$$

But when two molecules of nitric oxide combine with two atoms of oxygen to form nitric peroxide, the calorimetric equation is:

$$\underset{\text{Nitric oxide.}}{2'\mathbf{N}''O} + O_2 = \underset{\text{Nitric peroxide.}}{'\mathbf{N}_2O_4}, \quad . \; . \; . \; . \quad 34{,}000 \text{ cal.};$$

* It ought to be mentioned that the universal validity of the law of maximum work has been called in question. Some of the objections urged against the law have been successfully met by its author; but there are anomalies connected with the phenomena of heat of neutralization which do not appear capable of explanation on Berthelot's theory. (See more fully p. 115.)

or, the quantity of heat liberated is greater by 14,000 calories. Therefore, whenever an excess of oxygen is present, nitric peroxide ought to be formed. Not only is this the case, but nitrous anhydride combines directly with oxygen to form nitric peroxide:

$$\underset{\text{Nitrous anhydride.}}{N_2O_3} + O = \underset{\text{Nitric peroxide.}}{'N_2O_4}, \quad . \ . \ . \ . \quad 14{,}000 \text{ cal.},$$

On the other hand, hydrogen in combining with oxygen to form water yields:

$$H_2 + O = \underset{\text{Water.}}{OH_2}, \quad . \ . \ . \ . \ . \quad 69{,}000 \text{ cal.},$$

whereas, when these two elements unite to form hydroxyl, the effect is:

$$H_2 + O_2 = \underset{\text{Hydroxyl.}}{'O'_2H_2}, \quad . \ . \ . \ . \ . \quad 47{,}000 \text{ cal.},$$

giving a difference of 22,000 calories in favor of the lower oxide. When oxygen and hydrogen combine, water ought, therefore, to be formed, whilst hydroxyl ought to have a tendency to decompose into water and oxygen.

Furthermore, the formation of hydroxyl, starting from water and oxygen, ought to be accompanied by an absorption of heat. This compound cannot, therefore, be formed without the intervention of some foreign energy—for instance, that of a simultaneous chemical action.

There are several compounds, in the formation of which, starting from their elements, heat is absorbed. Such, for example, are the oxides of nitrogen, the oxides of chlorine, chloride of nitrogen, acetylene, cyanogen, etc.; and none of these can be produced by the mere interaction of their elements, acting by their intrinsic energy.

Acetylene, for example, is formed by the direct union of carbon and hydrogen; but this combination does not take place under the influence of chemical affinity alone: it requires the aid of the electric arc. The oxides of nitrogen are all derived from nitric peroxide, which can be formed from its elements only under the influence of intense heat (electric discharge, simultaneous combustion of hydrogen). The oxides of chlorine are produced by the action of chlorine on the alkaline oxides; but this is because their formation is accompanied by that of an alkaline chloride, the production of which is attended with liberation of much heat.

Decomposition.—A body that has been formed directly from its elements with liberation of heat will not spontaneously decompose; the intervention of external energy is necessary to separate its elements. Such forms of external energy are heat, light, electricity, a simultaneous chemical action and the energy of disaggregation developed by solution. The action of this last agent is displayed in the case of salts of weak acids, and those of certain feebly basic metallic oxides.

If, however, a compound be formed with absorption of heat, it will be capable of effecting its own decomposition. This is the case with the oxides of chlorine, which explode under the slightest disturbing influence; to this class belong chloride of nitrogen, ammonic nitrite, etc., bodies which decompose spontaneously at ordinary temperatures. When bodies formed with absorption of heat do not readily undergo spontaneous decomposition, they show a marked tendency to enter into direct combination or to undergo fresh chemical changes—such as polymeric condensation, breaking up into groups, complex decomposition—all of which changes are accompanied by liberation of heat. Bodies formed with absorption of heat are, moreover, particularly sensitive to the action of so-called *catalytic* or *contact* agents. Such agents do not in these cases usually introduce any special energy into a reaction; they merely serve to liberate a store of pre-existent potential energy.

Substitution.—Substitutions also take place according to the law of maximum work. Chlorine, in combining with hydrogen or the metals, liberates more heat than bromine, and bromine liberates more than iodine. Therefore bromine decomposes the iodides, expelling iodine, and forming bromides; chlorine decomposes both bromides and iodides, expelling bromine and iodine, and forming chlorides. In the same manner, whenever one metal displaces another from its salts, the formation of the new salt is attended with a greater liberation of heat. From this follows the well-known direct relation between the electromotive force of the metals and their heat of oxidation.

Double Decomposition.—In general one hydrated base displaces another from its salts, when it liberates more heat in combining with the same acids.* This is the case when the hydrates of the metals are precipitated by alkaline solutions. Thus:

$$\underset{\text{Plumbic nitrate.}}{\left\{\begin{matrix}\mathbf{NO_2}\\ \mathrm{Pbo''}\\ \mathbf{NO_2}\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2\mathrm{KHo}} = \underset{\text{Potassic nitrate.}}{2\mathbf{NO_2}\mathrm{Ko}} + \underset{\text{Plumbic hydrate.}}{\mathbf{Pb}\mathrm{Ho_2}}$$

This reaction liberates 12,200 cal. if all the compounds are in solution, and 45,600 cal. if they are in the solid state. In the same way, one acid expels another from its salts, when it liberates more heat in combining with the same base; at least, this is so in all cases where each of the acids forms only one salt with the base. But all these relations are only then strictly true, when the heat liberated by the acids, bases, and salts is calculated for these bodies in the same physical condition, namely, *the solid state.* The following example will show how a change of physical condition and the special combinations formed with the solvent may affect the result. Gaseous hydrochloric acid acts upon dry mercuric cyanide, forming mercuric chloride and hydrocyanic acid:

$$\underset{\text{Hydrochloric acid.}}{2\mathrm{HCl}} + \underset{\text{Mercuric cyanide.}}{\mathbf{Hg}\mathrm{Cy_2}} = \underset{\text{Hydrocyanic acid.}}{2\mathrm{HCy}} + \underset{\text{Mercuric chloride.}}{\mathbf{Hg}\mathrm{Cl_2}}\ .\ .\ + 10{,}600\ \text{cal.}$$

* See, however, p. 115.

But hydrocyanic acid in solution acts upon mercuric chloride in solution, forming mercuric cyanide and hydrochloric acid. This reversal of the reaction is explained by the fact that two molecules of hydrocyanic acid in solution liberate in acting upon mercuric oxide 31,000 cal., whilst a solution of hydrochloric acid liberates only 19,000 cal. There are therefore +12,000 cal. liberated in the reaction in the wet way, a result which experiment completely confirms. Theory, therefore, predicts this reversal of the reaction corresponding to the change in the thermal sign. This change is due to the intervention of a new chemical reaction attended by liberation of heat, the combination of gaseous hydrochloric acid with water, by which the hydrochloric acid has yielded up a portion of its energy.

The same principle of maximum work enables us to produce a number of compounds which could not be obtained directly, because their formation is attended with absorption, and their decomposition with liberation of heat. This end is attained by the device of a double decomposition bringing about the simultaneous formation of some other compound, the production of which is attended with a liberation of heat greater than the absorption first mentioned. For example, in the formation of hydroxyl from oxygen and water,

$$OH_2 + O = 'O'_2H_2 \ldots\ldots -21{,}800 \text{ cal.}$$

there is absorption of heat, and the reaction cannot therefore take place directly. In order to accomplish it, baric oxide is made to combine with oxygen, thereby liberating 11,800 cal.; and the baric dioxide thus obtained is acted on with dilute hydrochloric acid, forming baric chloride and hydroxyl, with liberation of 22,000 cal. more. The formation of baric chloride furnishes the supplementary energy which is employed in producing hydroxyl.

The rules given by Berthelot for the relation between the heat of neutralization of acids and bases, on the one hand, and their mutual affinity on the other, do not hold good in the case of solutions. In fact, the very reverse is frequently the case. Thomsen has made a series of careful determinations of the heat of neutralization of various acids and bases, and he shows that in mixed solutions of equal equivalents of two acids with a quantity of a base only sufficient for the neutralization of one, the larger portion of the base is frequently appropriated by that acid with which it evolves least heat in neutralization. This is in direct opposition to Berthelot's law of maximum work. Ostwald, by measuring the contraction or expansion which occurs on mixing solutions of acids and bases, has arrived at the same conclusion. It appears, therefore, that *the heat of neutralization cannot be regarded as a measure of affinity*. Thomsen shows that every base and every acid has a fixed *heat-equivalent*, which is liberated in its neutralization, and that the heat of neutralization in any given case is the sum of the heat-equivalents of acid and base. This follows from the fact that, if any two acids be neutralized with a given base, the *difference* between their heats of neutralization will be the same for their neutralization with

any other base, provided always that acids, bases, and salts in every case remain in solution. The same holds for the neutralization of bases with various acids: the *difference* between the heats of neutralization of any two bases with a given acid is the same for their neutralization with any other acid. It follows from this that *the heat of neutralization is independent of the degree of affinity between acid and base.* Ostwald has shown that a precisely similar law regulates the contraction or expansion which occurs when solutions containing equivalent quantities of acid and base are mixed: the *difference* in the degree of change of volume for any two acids with any given base is the same with any other base; each acid and each base produces its own definite and invariable change of volume, and the change of volume in any given case of neutralization is the sum of the changes for acid and base. The heat of neutralization appears to be greater the greater the contraction, or the smaller the expansion. Taking these facts together, the conclusion seems unavoidable that *the heat of neutralization is directly connected, not with chemical affinity, but with the changes which occur in the aggregation of the solution—expansion and contraction.*

The great obstacle to the interpretation of thermochemical data lies in the fact that, under the conditions of temperature at which calorimetric determinations are possible, there is no such thing as mere direct combination of elements. The thermal equation,

$$H + Cl = HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 22{,}000 \text{ cal.}$$

is a fiction. This equation ought to be written

$$H_2 + Cl_2 = 2HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 44{,}000 \text{ cal.}$$

and the thermal effect 44,000 cal. is in reality the algebraic sum of three distinct thermal effects—the heat absorbed by the separation of hydrogen from hydrogen, the heat absorbed by the separation of chlorine from chlorine, and the heat liberated by the union of hydrogen with chlorine. If the first of these be denoted by x, the second by y, and the third by z, we should have—

$$2z - (x + y) = 44{,}000 \text{ cal.}$$

Every thermal equation (except such as contain elements with monatomic molecules) is therefore a single equation with three unknown quantities, which are consequently undeterminable.

If hydrochloric acid could exist at a temperature at which the molecules of hydrogen and chlorine dissociate into single atoms, then the conditions of the first of the above thermal equations would be realized and x and y would be eliminated. But if there are such conditions, they lie far above the range of temperature at which such determinations are at present possible.

CHAPTER XVI.

FUSION AND FUSING-POINTS.

THE molecular changes which correspond to the passage of a body from the solid to the liquid state have already been discussed. As these changes depend on the energy of the molecules, and as this energy will be constant for any given body at a given temperature, it is evident that every substance which is fusible at all ought to have a fixed fusing-point, and such is, with few exceptions, the case. The use of the fusing-point as a means of identifying substances and testing their purity has also been described.

Change of Volume Accompanying Fusion. — Most substances in passing from the solid to the liquid state expand: the melted substance is the specifically lighter. With water and bismuth the reverse is the case; these bodies expand in solidifying. Thus, ice floats on the surface of water; and closed vessels, in which water is frozen, burst with the internal pressure.

Effect of Pressure in Altering the Fusing-point.—If a body expands in fusing, increase of pressure will tend to raise the fusing-point. In this case, the pressure acts counter to the energy of the molecules. The effect is very slight: according to Bunsen, a pressure of 156 atmospheres is necessary to raise the fusing-point of spermaceti from 47.7° C. to 50.9° C. If, on the contrary, fusion is accompanied by contraction, an increase of pressure will lower the fusing-point, the pressure in this case aiding the energy of the molecules. The effect in the case of water is a lowering of the fusing-point by .0075° C. for each atmosphere. Mousson succeeded, by means of very great pressure, in melting ice at —18° C.

Latent Heat of Fusion.—If a given weight of water at 100° C. be mixed with an equal weight of water at 0° C., the temperature of the mixture will be 50° C. If a given weight of water at 100° C. be mixed with an equal weight of powdered ice at 0° C., the temperature of the mixture will be only 10.4° C. If we suppose that, in this last case, a gram of each was taken (though in practice the experiment could not be accurately performed with such small quantities), the gram of water at 100° C. in cooling to 10.4° C. will have given off $100 - 10.4 = 89.6$ calories. But in giving off this quantity of heat, it has melted one gram of ice and raised the temperature of the resulting gram of water 10.4° C. This last rise of temperature will represent 10.4 calories. Therefore, as the heat given off is equal to the heat taken up:

$$\text{Melting of 1 gram of ice} + 10.4 \text{ cal.} = 89.6 \text{ cal.; or}$$
$$\text{Melting of 1 gram of ice} = 79.2 \text{ cal.}$$

In other words, when one gram of ice at 0° C. is converted into one gram of water of the same temperature, 79.2 calories—a quantity of heat sufficient to raise the temperature of an equal weight of water

79.2° C.—disappears. This quantity of heat is known as the *latent heat of fusion of ice*, or, as it is sometimes termed, the *latent heat of water.* The energy of motion represented by this latent heat is taken up by the molecules in some form which does not affect the thermometer: it occasions no rise of temperature, but only brings about a difference in the condition of the molecules in regard to each other, each molecule being enabled to overcome the attraction of its immediate neighbors, and to wander through the liquid.

All substances capable of assuming the liquid state possess latent heat of fusion. Water has the highest latent heat of all known liquids.

The disappearance of heat in the liquefaction of ice may be roughly shown by heating over a flame a vessel containing pieces of ice. As long as any ice remains unmelted, the temperature will rise very little above 0° C., all the heat which is taken up by the water being instantly employed in melting the ice. By first pounding the ice so as to increase the surface, and stirring continually so as thoroughly to mix the ice and water, the temperature of the whole may be kept at 0° C. As soon as the ice is melted, the temperature of the water will begin to rise as usual until the boiling-point is reached, when the temperature will again remain constant.

The heat which disappears when a body passes from the solid into the liquid state, is again evolved in the passage from the liquid to the solid state. (See *suspended solidification.*)

The cold which is produced by the solution of solids is attributable to the same cause. (See *solubility.*) In the process of solution, a solid in contact with its solvent may become liquid without the application of heat. Hence, when the latent heat of liquefaction of the solid disappears, the temperature of the whole is lowered, the heat of liquefaction being taken from the mass itself. This is the principle involved in *freezing-mixtures.* In such mixtures, the more rapid the process of solution or liquefaction without application of external heat, the greater is, *cæteris paribus*, the degree of cold attainable, there being less time for heat to be taken up from without. A mixture of 5 parts of ammonic chloride, 5 of potassic nitrate, and 19 of water, produces a reduction of temperature from + 10° to — 12° C. A solution of common salt in water freezes at a much lower temperature than pure water; if, therefore, salt be added to snow, the latter will melt. In this case there is simultaneous liquefaction of the snow and solution of the salt; but owing to the great latent heat of water, the cold is derived chiefly from the former source. A mixture of three parts of snow with one of common salt produces a cold of —22° C. If equal weights of snow and dilute sulphuric acid, previously cooled to — 7° C., be mixed, the temperature will sink as low as — 51° C.

The researches of Guthrie into the nature of the solid compounds which various salts form with water, have thrown great light upon the mode of action of freezing-mixtures and upon the degree of cold attainable by their means. Guthrie shows that all salts which are capable of dissolving in water form definite solid compounds with this solvent, and that every such compound has a fixed fusing-point. To the compounds of this class which are solid only at temperatures below 0° C.,

he has given the name *cryohydrates.* The same salt frequently forms more than one cryohydrate. Thus sodic chloride, which at —10° C. crystallizes with $2OH_2$, combines at a still lower temperature with 10.5 OH_2, yielding a compound fusing at — 22° C. The important law holds good that the fusing-point of that cryohydrate which is formed at the lowest temperature is the limit to the degree of cold attainable with a given freezing mixture, since any further abstraction of heat from the mixture occasions, not depression of temperature, but separation of the cryohydrate. Thus the greatest degree of cold which can be produced with a mixture of ice and sodic chloride is — 22° C. Further, the maximum effect from a freezing mixture is obtained when the ingredients are employed in the proportions requisite for the formation of the cryohydrate.

Suspended Solidification.—Although it is not possible (at least at ordinary pressures) to heat a substance a single degree above its fusing-point without producing liquefaction, yet many substances, when fused, may be cooled many degrees below their fusing-point without solidifying. This state, which is known as *suspended solidification*, is most readily produced in bodies from which air is excluded. Water inclosed in a small glass vessel from which the air has been removed may be cooled as low as — 8° or — 10° C. without solidifying. The fusing-point of phosphorus is 54° C.; but if melted under water, it may be cooled to 32° C. without becoming solid.

If a liquid body, thus cooled below its fusing-point, be touched with a portion of the same body in the solid state, solidification instantly ensues, and the temperature of the mass rises to the fusing-point. The cause of this rise in temperature is the latent heat of fusion, which is again evolved when the body passes back into the solid state. Solidification may also frequently be induced in such cases by agitation.

CHAPTER XVII.

EBULLITION AND BOILING-POINTS.

When the molecules of a liquid, in the course of their wanderings, reach the free surface of the liquid, they are carried by the force of their motion, should this happen to be in an upward direction, into the air. Here they behave like the molecules of a gas, striking against other molecules—either of the air or of their own kind—sometimes proceeding further upwards, sometimes being thrown back into the liquid. If the space above the liquid is unlimited, the molecules above the liquid will gradually wander away from it and no longer be exposed to the risk of falling into it again, whilst their place will be constantly taken by fresh molecules from the surface. This is the phenomenon of spontaneous evaporation at ordinary temperatures. If the space above the liquid is limited, the diffusion of molecules into it from the liquid will go on as before; but a point will be reached at which the number of

molecules which fall back into the liquid is as great as that of the molecules which leave its surface, upon which the evaporation will appear to cease, though in reality it is going on as before. The space is then said to be *saturated* with vapor. The quantity of vapor which will thus diffuse into a given space is constant for a given temperature and independent of the pressure. Thus at a given temperature the same quantity of vapor will diffuse into a vacuum and into an equal space containing air, the only difference being that the vacuum will fill more rapidly with vapor, as there are no molecules of air to oppose the passage of the molecules of vapor. This vapor exerts a pressure, and as this pressure must be proportional to the quantity of vapor present in the unit of space, it will also be constant for any given temperature. This pressure is known as the *tension* of the vapor of the liquid. Its action may be illustrated, and its amount measured, as follows: Two barometer-tubes are filled with mercury and inverted over a mercury trough. The mercury will stand equally high in both, and the height of the column will represent the pressure of the atmosphere. A few drops of water are now introduced into one of the tubes by allowing the water to rise through the mercury in the tube. In a very short time this column of mercury will show a marked depression, corresponding to the tension of the vapor of water for that temperature. If this barometer-tube be surrounded with a second wider tube, which can be filled with water of various temperatures, it will be noticed that as the temperature rises, the mercury in the barometer-tube sinks, corresponding to the increased vapor tension. The difference in height between the columns of mercury in the two barometer-tubes at any given temperature, will give the vapor tension of water for that temperature. When the temperature reaches 100° C., the boiling-point of water, the mercury inside and outside the tube with the water will stand at the same level—in other words, the tension of the vapor inside the tube exactly balances the pressure of the atmosphere. Hence the important law: *The temperature at which a liquid boils is that at which the tension of its vapor is equal to the atmospheric pressure.* The moment this point of equality is passed, the molecules from the surface of the liquid stream forth freely into space, carrying before them the layer of air which presses upon them. Bubbles of vapor are formed in the interior of the liquid, rise through it, and are discharged at its surface.

From the above law it follows, that by lowering the pressure, the boiling-point of a liquid may also be lowered. Water will boil in a vacuum at ordinary temperatures, if means be taken to absorb the aqueous vapor as quickly as it is formed. In like manner, by raising the pressure, the boiling-point may be raised. By heating water in a strong closed vessel, by which means the liquid is subjected to the pressure of its own vapor, the temperature may be raised far above 100° C. without causing ebullition. There is, however, for every liquid a fixed temperature beyond which no degree of pressure will suffice to restrain the liquid from passing into the gaseous state. This temperature is known as the *critical point*. If the liquid be heated in a very strong glass tube, the surface of the liquid, when the critical point is reached,

will be seen to disappear, and the whole tube will be filled with transparent vapor, almost of the same density as the liquid itself.*

The law that the tension of a vapor is constant for a given temperature and independent of the pressure, holds only for what are known as *saturated vapors*—vapors in contact with an excess of their liquids. When the space is not saturated with the vapor, and there is none of the liquid present from which a greater supply may be derived, the vapor behaves, in regard to temperature and pressure, like a true gas: for example, a forcible diminution of the volume would cause a corresponding increase in the pressure. In the case of a saturated vapor such a diminution of volume would only occasion a partial condensation of the vapor, the pressure remaining as before. Non-saturated vapors are also termed *superheated.*

When a liquid assumes the gaseous form, its molecules have to overcome, besides the pressure resting on the liquid, the force of cohesion, that is, of their mutual attraction. Hence anything which tends to increase the force of cohesion will raise the boiling-point of the liquid. As the attraction between the molecules of a substance and those of the liquid in which it is dissolved is greater than that of the molecules of the liquid for each other, it is clear that the presence of any solid substance in solution will increase the force of cohesion, and consequently raise the boiling-point of the liquid. Hence it is that aqueous solutions of salts boil above 100° C. The boiling-point of such solutions rises with the concentration.

The boiling-point of a liquid is best ascertained by means of a thermometer immersed *in the vapor* of the liquid. The temperature at which the *liquid* enters into ebullition varies with the nature of the vessel in which it is contained; but the temperature of its vapor or steam is constant. Water boils in a glass vessel at a higher temperature than in a vessel of iron, owing to the greater adhesion between water and glass, which hinders the formation of bubbles of steam at the points of contact of the liquid and the vessel. By heating in a glass vessel water from which the air had been previously expelled by boiling, the temperature may be raised several degrees above 100° C. without ebullition supervening. When this state of molecular inertia is from any cause disturbed, ebullition suddenly commences with explosive violence, and the temperature sinks to 100° C. Liquids thus heated above their boiling-points are said to be *superheated*, and the phenomenon of sudden percussive ebullition is commonly known as *bumping.*

Various attempts have been made to discover some law connecting the boiling-point of a liquid with its constitution or molecular weight. Such laws as have been deduced hold only for compounds belonging to the same group, and generally only for a few members of

* According to Ramsay, however, the critical point is merely the temperature at which the liquid in the tube has the same specific gravity as its vapor, and a gas may be liquefied at any temperature, provided sufficient pressure be applied.

such a group. Moreover, the correspondence between experiment and theory is seldom more than approximate. A very few examples will suffice. The normal alcohols of the general formula $\mathbf{C}_nH_{2n+1}Ho$ display among their lower members a difference of boiling-point amounting to about 19.5° C. for every difference of CH_2 in the molecular formula. For a similar difference of CH_2 in the normal fatty acids of the general formula $\mathbf{C}_nH_{2n+1}(\mathbf{C}OHo)$, the difference of boiling-point is about 22° C. The difference becomes, in the case of the acids, rapidly less for the higher members.

Normal alcohols.		Boiling-point.	Difference.
Ethylic alcohol,	$\mathbf{C}_2H_5Ho$	78°	
Propylic "	$\mathbf{C}_3H_7Ho$	97.4	19.4
Butylic "	$\mathbf{C}_4H_9Ho$	116.9	19.5
Amylic "	$\mathbf{C}_5H_{11}Ho$	137	20.1
Hexylic "	$\mathbf{C}_6H_{13}Ho$	157.5	20.5
Heptylic "	$\mathbf{C}_7H_{15}Ho$	176	19.5

Normal fatty acids.		Boiling-point.	Difference.
Acetic acid	$\begin{cases} \mathbf{C}H_3 \\ \mathbf{C}OHo \end{cases}$	118°	
Propionic acid	$\begin{cases} \mathbf{C}_2H_5 \\ \mathbf{C}OHo \end{cases}$	140.7	22.7
Butyric acid	$\begin{cases} \mathbf{C}_3H_7 \\ \mathbf{C}OHo \end{cases}$	163	22.3
Valeric acid	$\begin{cases} \mathbf{C}_4H_9 \\ \mathbf{C}OHo \end{cases}$	184.5	21.5
Caproic acid	$\begin{cases} \mathbf{C}_5H_{11} \\ \mathbf{C}OHo \end{cases}$	205	20.5
Œnanthylic acid	$\begin{cases} \mathbf{C}_6H_{13} \\ \mathbf{C}OHo \end{cases}$	223.5	18.5
Caprylic acid	$\begin{cases} \mathbf{C}_7H_{15} \\ \mathbf{C}OHo \end{cases}$	236.5	13
Pelargonic acid	$\begin{cases} \mathbf{C}_8H_{17} \\ \mathbf{C}OHo \end{cases}$	253.5	17

Latent Heat of Vapors.—It has already been mentioned that bodies, in passing from the solid to the liquid state, take up heat without exhibiting any rise of temperature, the heat which thus disappears being employed in producing a change in the molecular condition. The same phenomenon is observed in a still more marked degree during the passage from the liquid to the gaseous state. If two thermometers be introduced into a flask of water boiling over a flame, one being plunged in the liquid, the other suspended in the steam, both will register the same temperature, 100° C. (The themometer in the liquid may happen to be a fraction of a degree higher; see *Boiling-points.*) This temperature will be preserved by both thermometers, as long as there is any liquid left, though all the time heat is being communicated to the water. The heat which thus disappears in causing a change of molecular condition, is known as the *latent heat of steam,* and is evolved

again in exactly the same quantity when the steam is condensed. This last fact is turned to account in the determination of the latent heat of steam. If steam be passed into a kilogram of water at 0° C. till the temperature of the latter reaches 100° C., it will be found that the weight of the water has increased to 1.186 kilograms; in other words, 0.186 kilogram of steam at 100° C., in being converted into water at 100° C., gives off heat sufficient to raise the temperature of 1 kilogram of water through 100° C.; therefore, 1 kilogram of steam will raise 5.37 kilograms of water through 100° C. or 537 kilograms through 1° C.; or 1 *gram of steam will raise* 537 *grams of water through* 1° *C. The latent heat of steam is therefore* 537 *calories.*

Steam has the highest latent heat of all known vapors. It is this which renders it such a valuable heating agent when the heat has to be carried to a distance from its source.

The phenomena of latent heat, both of liquids and vapors, were first observed and studied by Black.*

Liquefaction of Gases.—The fact that the non-saturated or superheated vapors of liquids behave like true gases leads naturally to the converse idea that the gases may be nothing more that the superheated vapors of liquids unknown under ordinary conditions of temperature and pressure. There are two methods of condensing a vapor to a liquid, one being refrigeration, and the other pressure; pressure having, as we have already seen, the effect of raising the boiling-point of the liquid. This last method was that chiefly employed by the earlier experimenters in this field, of whom Faraday may be mentioned as the chief. Faraday's earlier method consisted in generating the gas to be liquefied from some suitable substance contained in one of the limbs of a bent sealed glass tube. The other limb was immersed in cold water, and in this extremity of the tube the gas, liquified by its own pressure, condensed. In this way Faraday succeeded in liquifying chlorine, cyanogen, ammonia, and some other gases. In his later experiments, however, he combined cold with pressure, and thus liquefied carbonic anhydride, nitrous oxide, and other gases. There were, however, a number of gases—oxygen, hydrogen, nitrogen, carbonic oxide, nitric oxide, and marsh-gas—which till quite lately defied all efforts to reduce them to the liquid state. The reason of this was, that the earlier experimenters relied chiefly on pressure to produce liquefaction, and it was not till the discovery of the phenomenon of the *critical point* by Andrews, that it became evident that at ordinary temperatures no amount of pressure could liquefy these gases.† Now, however, by the united agency of intense cold and enormous pressure, the problem has

* The expression "latent heat," though still in very general use, must be regarded as a survival, as it no longer expresses the views of physicists regarding this phenomenon. The heat which has disappeared *as such* in the above process is no longer *heat*, and ought not, properly speaking, to be called by this name. It has performed the work of overcoming cohesion; it is no longer present in that form of molecular vibration recognizable as heat, and possibly exists only as the potential energy of position of the molecules. It would be just as admissible to apply the epithet "latent" to the heat which disappears when a steam-engine is employed to raise a weight, because the potential energy of the raised weight can be reconverted into heat.

† See, however, p. 121, footnote.

been solved simultaneously by two workers in this field, MM. Pictet and Cailletet. (See *Hydrogen.*) To give an idea of the difficulties to be surmounted in these experiments, it will suffice to mention that oxygen required a pressure of 300 atmospheres and a temperature of —110° C. (—166° F.), for its liquefaction,* and that hydrogen did not succumb till a pressure of 650 atmospheres, coupled with a temperature of —140° C. (—220° F.), had been reached.

In the descriptions of the various gases the temperatures and pressures of liquefaction will be given.

CHAPTER XVIII.

SOLUTION.

SOLUBILITY is the property which many substances—gaseous, liquid, and solid, possess of mixing homogeneously with some liquid employed as a *solvent.* Gaseous and solid bodies, when in solution, assume for the time being the liquid state.

Solubility of Gases.—The solubility of gases is known as *absorption.* Some gases, such as hydrogen and nitrogen, are soluble in water to a very slight degree only ; others, like carbonic anhydride, chlorine, and sulphuretted hydrogen, are dissolved in moderate quantity ; whilst others again, like hydrochloric acid and ammonia, are extremely soluble, the volume absorbed being in the case of the last-mentioned gas at 0° more than a thousand times that of the water employed. In the case of gases slightly or only moderately soluble, the quantity absorbed is approximately proportional to the pressure. This fact may be accounted for by the assumption that the gas occupies the spaces between the molecules of the liquid as it would any other empty space: the quantity which can be pressed into this space will then be proportional to the pressure. The solubility generally decreases as the temperature rises. Hence this law may be expressed by saying that the *volume* of these gases absorbed is constant for a given temperature, being less for higher temperatures, and independent of the pressure. For those gases which are very soluble, this law does not hold. In these cases, the solubility is the result of a powerful affinity between the molecules of the gas and those of the solvent. Such absorptions are accompanied by great evolution of heat—partly the latent heat of the gas, partly the heat of chemical combination.

Solubility of Liquids—Miscibility.—The following views on solubility have been enunciated by Dossios: Let there be two liquids A and B, and let the single molecules of each be represented by a and b respectively, and let the attraction of similar molecules be expressed by aa, bb,

* According to the still more recent results of Wroblewski and Olzewski, oxygen liquefies at the somewhat lower temperature of —136° under a pressure of only 22.5 atmospheres.

and that of dissimilar molecules by *ab*. Then if *ab* be greater than *aa* + *bb*, the liquids will obviously be miscible in all proportions. But if *ab* be less than *aa* + *bb*, the attraction *ab* can effect the mixture of the two liquids only with the aid of the energy of their molecules. At the surface of separation of the two liquids, single molecules of *A* will sometimes be carried, by the force of their own motion, among the molecules of *B*, where they will wander about until they happen again to reach the surface of separation, when they will for the most part be retained by the other molecules of *A*. At length a condition will be reached in which as many molecules *a* return to *A* as leave it, and as this is the case, *B* is saturated with *A*. The same holds in regard to the saturation of *A* with *B*. Two such liquids will dissolve in each other only up to a certain point. An example of this is afforded by the behaviour of ether and water towards each other. If equal volumes of these liquids be agitated together, the ether dissolves about $\frac{1}{35}$ of its bulk of water, whilst the water takes up $\frac{1}{8}$ of its bulk of ether.

When two liquids are miscible in all proportions, the force which comes into play is the preponderating attraction of dissimilar molecules. The heat which is liberated by the approximation of these dissimilar molecules will therefore be greater than that absorbed in the separation of similar molecules. Hence, in most cases where two liquids are miscible in all proportions, heat is evolved by their mixture. A remarkable exception to this rule is presented by a mixture of equivalent proportions of ethylic oxalate and amylic iodide, a depression of temperature amounting to 9.3° occurring when the liquids are suddenly blended.

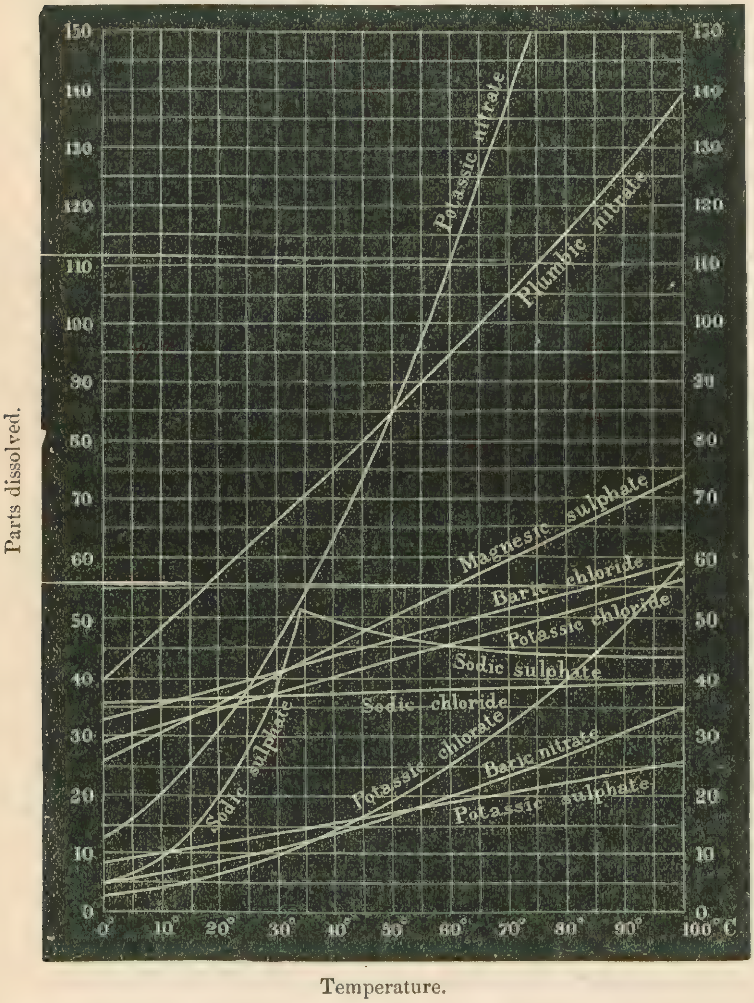
Solubility of Solids.—Let *A* be a solid body, and *B* a liquid, and let the single molecules and their attractions be designated as above. Then the forces which strive to prevent solution will be *aa* and *bb*, those which tend to induce it, *ab*, and the energy of the molecules. The attraction *ab* must be less than *aa*, otherwise the liquid and the solid would form a solid compound. The molecules *a* are carried away from *A* by their energy, plus the attraction *ab*, wander through the liquid and sometimes return to *A*. When as many molecules return to *A* in unit of time as leave it, the solution is saturated. As the projection of the molecules of *A* among those of *B* is dependent in part on the molecular energy, it is evident that the solubility will increase with the temperature. This is generally found to be the case; the cause of some apparent exceptions to this rule will be mentioned later.

The diagram (p. 126) is a graphic representation of the relations between temperature and solubility in the case of various salts, the solvent being water. The abscissæ express the temperatures; the ordinates, the number of parts of anhydrous salt soluble in 100 parts of water.

The method of using this diagram will be evident on inspection. Thus at 0° C., 100 parts of water dissolve 26 parts of magnesic sulphate; at 40° C., 45 parts; at 100°, 74 parts. As the increase of solubility of magnesic sulphate is proportional to the increase of temperature, the line representing its solubility will be straight. The more

rapid the increase of solubility in a salt, the more its curve will approach the vertical; the slower this increase, the more nearly horizontal the curve will be. In the case of sodic chloride, which is almost equally soluble at all temperatures, the curve is nearly horizontal. If the solubility increases more rapidly than the temperature, the curve will show this by bending upwards. In the case of potassic nitrate

FIG. 1.—SOLUBILITY OF SALTS IN 100 PARTS OF WATER.



and plumbic nitrate the solubility at 0° of these two salts in 100 parts of water is 13 and 40 parts respectively; at 45° C., both salts are equally soluble, 100 parts of water dissolving 85 parts of each; whilst at 73° C., the solubility of potassic nitrate is 150 parts against 108 parts of plumbic nitrate. Thus, by rise of temperature, the relative

solubilities of these two salts have been reversed, the more soluble becoming the less soluble. This is shown in the diagram by the intersection of the curves. The point of intersection indicates the temperature of equal solubility.

The solubility of sodic sulphate presents a singular anomaly. At 0° C., the solubility in 100 parts of water is 5 parts; it increases more rapidly than the temperature, till at 33° C., it is 51 parts; then it suddenly decreases, and goes on decreasing the higher the temperature rises. This anomaly would be quite inexplicable, if we were forced to assume that it is the same body which is contained in the solution above and below 33° C.; but closer examination shows this assumption to be unnecessary. Below 33° C., the solution deposits crystals of the formula $\mathbf{S}O_2Nao_2,10\mathbf{O}H_2$; above this temperature the salt which separates out possesses the formula $\mathbf{S}O_2Nao_2,\mathbf{O}H_2$.* The latter salt is less soluble than the former, hence the change in the solubility. The higher the temperature, the greater the quantity of $\mathbf{S}O_2Nao_2,10\mathbf{O}H_2$ which dissociates into $\mathbf{S}O_2Nao_2,\mathbf{O}H_2$ and water. There is no difficulty in conceiving that a salt may exist in different states in its solutions, at one time with more, at another time with less water of crystallization. Anhydrous cobaltous chloride is blue, as is also the aquate $\mathbf{Co}Cl_2,2\mathbf{O}H_2$; whilst the aquate $\mathbf{Co}Cl_2,6\mathbf{O}H_2$ is pink, and dissolves in water with this color. If to a concentrated aqueous solution of the pink salt a dehydrating agent—strong hydrochloric acid, or absolute alcohol—be added, the solution becomes blue. If less alcohol be added, the solution remains pink in the cold; but on heating, the color changes to blue, and on cooling returns to pink again. Here we have a dissociation perfectly analogous to that of the higher aquate of sodic sulphate, the presence of the anhydrous cobaltous chloride (or of the lower aquate) being denoted by the change of color in the solution.

Solution is almost invariably attended with contraction, the volume of the substance dissolved, together with that of the solvent, being greater than that of the resulting solution. The only known exception among anhydrous salts occurs in the case of ammonic chloride, the solution of which is accompanied by expansion. The most marked contraction is displayed by dehydrated salts which form definite compounds with water. Contraction also takes place when a solution of a substance is further diluted with the solvent.

Solution is attended with absorption of heat. In those cases in which heat appears to be liberated, the substance enters into definite chemical combination with the solvent, in which process heat is evolved. The compound thus formed dissolves with absorption of heat. The excess of thermal effect due to chemical combination produces the rise of temperature. Caustic potash (KHo) dissolves in water with liberation of great heat. But the crystalline aquate $KHo,2\mathbf{O}H_2$, which is obtained by cooling a concentrated solution of caustic potash, dissolves in water with absorption of heat.

The absorption of heat which attends solution is for the most part attributable to the latent heat of liquefaction of the substance (see *Latent*

* Generally stated to be anhydrous. See, however, Thomsen, *Deut. chem. Ges. Ber.*, 11, 2042.

Heat of Fusion). It is difficult to give an exact account of the various thermal items which go to make up the total thermal effect of solution, as the process is of a complex nature. The explanation formerly in vogue, according to which the fall of temperature during solution is entirely due to the latent heat of liquefaction of the substance, solution itself being caused by the excess of affinity of solvent for substance over that of substance for substance *plus* that of solvent for solvent, is manifestly untenable. According to this explanation, solution itself would always be accompanied with liberation of heat, the absorption of heat which is observed being attributable to the excess of heat which becomes latent in the liquefaction of the substance. The absorption of heat during solution would therefore be less than the latent heat of fusion. But very often the reverse is the case. The latent heat of fusion of 1 gram of potassic nitrate is 49 calories; but by dissolving the same weight of this salt in 20 grams of water at 20° C., 81 calories are absorbed.

Supersaturation or Suspended Crystallization.—When a solution contains at a given temperature more salt than the coefficient of solubility of that salt indicates, the solution is said to be *supersaturated*, or the crystallization is said to be suspended. The phenomenon is analogous to that of suspended solidification, observed in the case of fused solids. It occurs most readily with salts which form more than one aquate, and is unknown in the case of anhydrous salts. It may be induced by dissolving, with the aid of heat, a salt which has a tendency to form a supersaturated solution, and allowing the *clear* liquid, which must be free from undissolved substance, to cool, excluding dust. On dropping into such a solution a crystal of the aquate which would be formed at that temperature, crystallization immediately ensues with elevation of temperature, the latent heat of liquefaction being evolved. A salt well suited for this experiment is sodic sulphate. No other aquate or modification of a salt than the one which is formed at the given temperature will induce crystallization; thus sodic sulphate of the formula $\mathbf{S}O_2Nao_2,\mathbf{O}H_2$, crystallized above 33° C., may be added to a supersaturated solution of sodic sulphate at ordinary temperatures without effect; whilst the addition of the smallest fragment of the aquate $\mathbf{S}O_2Nao_2,10\mathbf{O}H_2$ causes instantaneous crystallization.

CHAPTER XIX.

DIFFUSION.

If water be carefully poured on a concentrated solution of a salt contained in a tall glass vessel, the liquids will be seen to form two distinct layers, the specifically heavier solution of the salt remaining at the bottom. After standing for some time, however, the salt will be found to be equally distributed throughout the liquid. If a solution of a colored salt, such as cupric sulphate or potassic dichromate, be employed, the progress of this distribution or *diffusion*, as it is termed, will be rendered

visible to the eye by a gradation of shades, extending from the bottom to the surface of the liquid, and ranging through every intermediate tint from the color of the concentrated solution to absolute colorlessness. At last, when the process of diffusion is complete, the liquid will exhibit a uniform tint throughout.

In like manner, if two tall glass vessels be placed mouth to mouth, one over the other, and separated by a glass plate, the upper being filled with air and the lower with chlorine, then, if the glass plate be carefully withdrawn, the lower vessel will be seen to be filled with the yellowish-green chlorine, whilst the gas in the upper vessel is colorless. But after a short time, the yellowish-green color will begin to extend into the upper vessel, and this will continue until the entire gas presents one uniform tint. The upward progress of the chlorine may further be made visible by the gradual bleaching of a strip of moist carmine-paper attached to the inside of the upper vessel and extending from top to bottom.

In both these cases, the force of diffusion is sufficient to overcome the counteracting force of gravity. The heavier molecules of the salt find their way upwards through the lighter molecules of the water; the latter penetrates downwards, diluting the concentrated solution. Chlorine is nearly two and a half times heavier than air; yet its molecules gradually rise through those of the oxygen and nitrogen of the air, whilst the latter find their way into the lowest parts of the vessel. In both experiments the ultimate result is uniform mixture.

This *diffusion* has its source in the independent motions of the molecules. These motions have already been referred to on various occasions in this introduction, while discussing the gaseous and liquid states of matter.

The phenomena of diffusion were first thoroughly investigated by Graham, to whom is due the deduction of various important laws in regard to this subject.

Diffusion of Liquids.—The quantities of a salt which pass in equal times from a solution into the adjacent water are proportional to the weight of salt originally in solution. (This law does not hold for very concentrated solutions.)

Rise of temperature increases the velocity of diffusion. This must evidently be the case, as the velocity with which the molecules move increases with the temperature.

Different substances have different velocities of diffusion. Isomorphous salts frequently possess equal velocities of diffusion.

Mixed solutions of salts, which do not act chemically on each other, do not diffuse at the same rates as when separate, the difference in their rates of diffusion being increased by mixture. Double salts may frequently be decomposed by means of the unequal velocity of diffusion of their component single salts.

Dialysis.—In the course of his investigations on the diffusion of liquids, Graham made the remarkable discovery that certain substances when in solution diffuse through porous membranes, such as bladder or parchment, whereas others do not possess this property. He found further, that the substances which thus diffuse are always crystallizable,

whereas those which are unable to pass through the membrane are amorphous. He thus divided all substances into *crystalloids* and *colloids* (from *κόλλα*, glue), and founded upon the above observations a method of separating these two classes of substances. This method, to which he gave the name of *dialysis*, is carried out as follows: A piece of bladder or parchment paper is tied tightly over the bottom of a glass cylinder open at both ends. The liquid to be dialyzed is poured into the cylinder, so as to rest on the membrane, the lower surface of which is kept in contact with water. The crystallizable substance diffuses freely through the membrane and mixes with the water, whilst the colloid remains in the cylinder. By constantly changing the external water, a pure solution of the colloid may be ultimately obtained.

The explanation of the phenomenon is as follows: The porous membrane, although itself insoluble, takes up water. This may be shown by the great increase in bulk which a piece of bladder undergoes when placed in water. Through the medium of this absorbed water the molecules of the crystalloid are enabled to diffuse. It is possible that the molecules of colloids, on the other hand, are much larger, or are aggregated into small masses, so that they are unable to pass through the pores of the membrane.

The membrane must itself be a colloid. Dialysis has been performed with an artificial membrane of amorphous silicic acid.

Diffusion of Gases.—Gases may diffuse either freely into each other, as in the experiment already mentioned, or through very fine openings. A porous diaphragm of gypsum or compressed graphite constitutes a system of such fine openings. Owing to the exceedingly small dimensions of the molecules of a gas, they pass through the pores of such a diaphragm almost unimpeded. The law of free diffusion, and of diffusion through diaphragms, is the same, and may be stated to be as follows: *The velocities of diffusion of any two gases are inversely as the square roots of their densities.* Thus the densities of hydrogen and oxygen are as 1 : 16, and their velocities of diffusion are as 4 : 1. The kinetic theory of gases informs us that the mean velocities of the molecules of any two gases are inversely proportional to the square roots of their densities. The above law may therefore also be expressed: *The velocities of diffusion of any two gases are directly as the mean velocities of their molecules.* The extreme velocity with which hydrogen diffuses may be well shown by the following experiment: A tube, closed at the upper end with a thin plate of gypsum, is filled with hydrogen, and the lower end is plunged into water. Since the hydrogen passes out through the pores of the gypsum much more rapidly than the air can enter, the water rises in the tube.

The degree of agreement between theory and experiment for the above law will be seen from the following table, which contains determinations of the velocities of diffusion of some of the commoner gases. In these experiments the gas to be examined was contained in a tube, closed at one end with a porous plug of gypsum, and at the other with mercury or water, according to the nature of the gas. The quantity of the gas which escaped through the porous diaphragm, and the quantity of air which entered, were carefully determined. In this way it was

found that if the density of a given gas, referred to air as unity, be d, then the volume of this gas which diffuses in the same time as one volume of air, is equal to $\sqrt{\frac{1}{d}}$, as expressed in the foregoing law. This calculated value is given in the third column, and the observed volume in the fourth column of the table:

Name of gas.	Density of gas $= d$. (Air $= 1$.)	$\sqrt{\frac{1}{d}}$	Volume of gas which diffused in the same time as one volume of air.
Hydrogen, ...	0.0694	3.7947	3.83
Methylic hydride, ...	0.555	1.3414	1.344
Ethylene, ...	0 972	1.0140	1.0191
Carbonic oxide, ...	0.972	1.0140	1.0149
Nitrogen, ...	0.972	1.0140	1.0143
Oxygen, ...	1.111	0.9487	0.9487
Sulphuretted hydrogen, . .	1.1805	0.9204	0.95
Nitrous oxide, ...	1.527	0.8091	0.82
Carbonic anhydride, . . .	1.527	0.8091	0.812
Sulphurous anhydride, . .	2.222	0.6708	0.68

CHAPTER XX.

CRYSTALLOGRAPHY.

When a solid separates from its solution, or when a fused or vaporous substance solidifies, the molecules frequently arrange themselves in definite geometrical forms, known as crystals. A crystal is a polyhedron, more or less symmetrical, bounded by plane surfaces which intersect at definite angles. Crystals possess not only external, but also internal structure, their internal structure frequently causing them to exhibit a definite cleavage parallel to certain faces of the crystal. Mica, calcite, and fluor spar are instances of very perfect cleavage. As some of the faces of a crystal are generally impeded in their growth, crystals seldom attain to their ideal, or symmetrical development; but as the faces always grow in planes parallel to themselves, the value of the angles remains constant. In measurements of crystals, it is consequently only the value of the angles which is regarded, and from these the ideal form of the crystal may be constructed by geometrical methods.

Substances which thus spontaneously assume definite external form, are said to be *crystallized*. Those solids which are devoid of all crystalline structure are termed *amorphous*. Glass and resin are instances of amorphous bodies.

The crystalline form assumed by a substance may be either simple or compound, according as the faces are of one or of more than one kind. Every compound form may be resolved into the two or more simple forms of which it is compounded.

In a compound crystal, the form which possesses the largest faces,

and which consequently determines the character of the crystal, is termed the *dominant form*, the others are the *subordinate forms*.

The various simple forms which occur in any compound crystal belong to one and the same system. Six systems of crystals are recognized, and to one or other of these all crystals may be referred. These systems are distinguished according to the mode of arrangement of certain imaginary lines or *axes*, which intersect and bisect each other in one point, and are supposed to be drawn between two opposite solid angles, or between the central points of two opposite surfaces or of two opposite edges of the crystal.

The following is a list of the various systems, with the arrangement of the axes peculiar to each:

1. The *regular system*. Three equal axes, intersecting at right angles.
2. The *quadratic system*. Three axes intersecting at right angles. Two of the axes are equal; the third is longer or shorter than the other two, and is termed the *principal axis*.
3. The *rhombic system*. Three unequal axes intersecting at right angles.
4. The *monoclinic system*. Three unequal axes. Two intersect obliquely, and the third is perpendicular to their plane.
5. The *triclinic system*. Three unequal axes which intersect obliquely.
6. The *hexagonal system*. This system has four axes. Three equal axes lie in one plane, and intersect at angles of 60°; the fourth, or *principal axis*, is longer or shorter, and is perpendicular to this plane.

In each system that form of crystal, in which the faces intersect all three axes at their normal length, is known as the *fundamental form*. In the first five systems, the fundamental form is an octahedron, differing for each system; in the sixth, or hexagonal system, it is a dihexahedron, or double six-sided pyramid. All other forms which occur in a system are derived from the fundamental form by variation of the relative length of the axes. A very simple law governs this variation. If the half-lengths of the three axes be represented by a, b, and c, respectively, then these three values will express the distances from the point of intersection of the axes at which the axes are cut by any plane which can constitute one of the faces of the fundamental form. The fundamental form is therefore designated by the ratio, $a : b : c$. In the derived forms, either one or two of these values may be varied by some rational multiple, which may be either an integer or a fraction, but will seldom be complex: thus derived forms may occur in which the ratio of the semi-axes is $a : 2b : 2c$, or $a : b : 3c$, or $a : \frac{1}{2}b : \frac{1}{4}c$, or any other ratio derived by some such simple process from the ratio of the fundamental form.

1. *Regular System.*—The fundamental form is the regular octahedron (Fig. 2). This form is inclosed by eight equilateral triangles; it has twelve equal edges, with an angle of 109° 28′ 16″, and six equal four-plane solid angles. The three equal and right-angled axes terminate in the solid angles. The ratio for this form is $a : a : a$. (Examples: *alum, magnetic iron ore.*)

A second form of the regular system is the cube (Fig. 3). It has six equal square faces, twelve equal right-angled edges, and eight equal

three-plane solid angles. The three equal and right-angled axes terminate in the centres of the faces. Each face consequently intersects one axis at its normal half-length a, and lies parallel to the other two axes, or, as this is expressed in crystallographical terminology, intersects them at an infinite distance. The ratio of this form is, therefore,

FIG. 2.

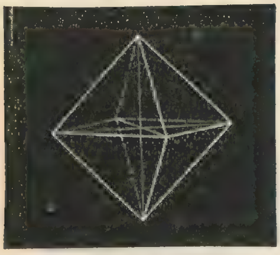
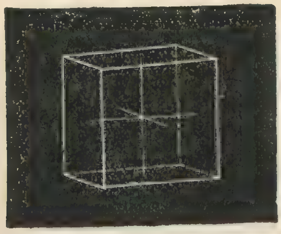


FIG. 3.

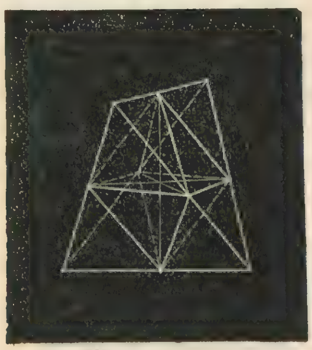


$a : \infty : \infty$. In combination the octahedron cuts off the solid angles of the dominant cube, and the cube cuts off the solid angles of the dominant octahedron. (Examples of cube: *rock salt*, *fluorspar*.)

A third form is the rhombic dodecahedron (Fig. 4). It has twelve equal rhombic faces, twenty-four equal edges with angles of 120°, eight equal three-plane solid angles (corresponding in position to the solid angles of the cube), and six equal four-plane solid angles (corresponding to those of the octahedron). The three equal and right-angled axes

FIG. 4.

FIG. 5.



terminate in the four-plane solid angles. Each face intersects two of the semi-axes at the normal distance a; the third at an infinite distance. The ratio of this form is therefore $a : a : \infty$. (Example: *garnet.*) In combination, the dodecahedron cuts off the edges of the octahedron and of the cube; whilst the cube cuts off the four-plane solid angles, and the octahedron the three-plane solid angles of the dodecahedron.

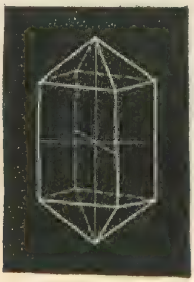
Hemihedral Forms of the Regular System.—Hemihedral forms are such as would be generated by supposing the alternate faces of a crystal to extend till the other alternate faces disappear. In this way the regular tetrahedron (Fig. 5) may be developed from the octahedron. (In the

figure the octahedron is drawn inside the tetrahedron.) In combination with a dominant cube, the tetrahedron cuts off alternate solid angles of the cube, as in the case of the mineral *boracite*.

2. *Quadratic System.*—The fundamental form of this system is the *quadratic octahedron* or double four-sided *pyramid* with square base (Fig. 6). It is inclosed by eight isosceles triangles, through the vertices

FIG. 6.

FIG. 7.



of which the principal axis passes. The edges are of two kinds, vertical and lateral; the vertical and lateral solid angles are also distinct. (Example: *copper pyrites.*)

Another form is the *prism of the first order*, the four faces of which intersect the two secondary axes at the normal distance and lie parallel to the principal axis. This prism is inclosed at both ends, either by a terminal plane which intersects the principal axis at right angles, or by the quadratic octahedron, as in Fig. 7.

3. *Rhombic System.*—The fundamental form is the rhombic octahedron, or double four-sided pyramid with rhombic base (Fig. 8). It is inclosed by eight scalene triangles. The edges are of three kinds, and

FIG. 8.

FIG. 9.

there are also three kinds of solid angles. In this system there are three prisms which run parallel to the three axes. That which is parallel to the longest or principal axis, is termed the *prism*, and is placed vertically; the other two, which are parallel to the two secondary axes, are termed *domes*, and cross each other at right angles in the horizontal plane. There are also three different terminal planes, which are re-

spectively perpendicular to the three axes. *Sulphur*, either native or crystallized from solutions, belongs to the rhombic system.

4. *Monoclinic System.*—The fundamental form would be a double pyramid with rhombic base (Fig. 9), in which the axis of the pryamid is inclined obliquely to the base. This is, however, a compound form, as it is composed of two distinct sets of four faces each, one of which sets frequently occurs in combination without the other. There is, in fact, in this system, no *single* form which can inclose space. (Examples: *gypsum, hornblende.*)

5. *Triclinic System.*—In this system, parallel and opposite pairs of faces only are equal. The octahedron (Fig. 10) is therefore a combi-

FIG. 10.

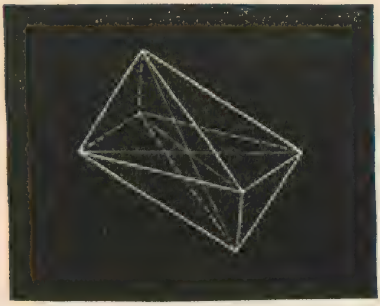


FIG. 11.

nation of four pairs of faces, any of which pairs may occur in compound forms without the others. This is the least symmetrical of all the systems. *Cupric sulphate* is triclinic.

6. *Hexagonal System.*—The fundamental form is the double six-sided pyramid (Fig. 11). It is inclosed by twelve isosceles triangles, of which the vertices terminate in two groups of six each in the ends of the principal axis. The lateral edges form a regular hexagon. Fig. 12 shows this form in combination with the hexagonal prism of the first order as it occurs in quartz.

FIG. 12.

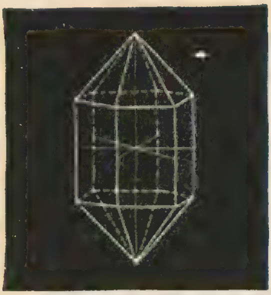


FIG. 13.

The most important of the hemihedral forms of the hexagonal system is the *rhombohedron*, which is derived from the double six-sided pyramid by the development of alternate faces. Fig. 13 shows the

principal rhombohedron of calcite. The rhombohedron is inclosed by six rhombic faces. It has six vertical edges, which unite in two groups of three each in the ends of the principal axis; and six lateral edges, which form a zig-zag line round the crystal, and in the middle points of which the secondary axes terminate. The sum of the angles of a lateral and a vertical edge is always equal to two right angles.

CHAPTER XXI.

WEIGHTS AND MEASURES.

THE weights and measures employed in this book are chiefly those of the French decimal system, founded upon the metre, which is $\frac{1}{10,000,000}$th part of a quadrant of a great terrestrial circle. The following tables, published by Messrs. De La Rue and Co., will enable the student to convert these into their English equivalents whenever it may be necessary.

French Measures of Length.

	In English inches.	In English feet = 12 inches.	In English yards = 3 feet.	In English fathoms = 6 feet.	In English miles = 1760 yds.
Millimetre, ...	0.03937	0.003281	0.0010936	0.0005468	0.0000006
Centimetre, ...	0.39371	0.032809	0.0109363	0.0054682	0.0000062
Decimetre, ...	3.93708	0.328090	0.1093633	0.0546816	0.0000621
Metre, ...	39.37079	3.280899	1.0936331	0.5468165	0.0006214
Decametre, ...	393.70790	32.808992	10.9363310	5.4681655	0.0062138
Hectometre, ...	3937.07900	328.089920	109.3633100	54.6816550	0.0621382
Kilometre, ...	39370.79000	3280.899200	1093.6331000	546.8165500	0.6213824
Myriometre, ...	393707.90000	32808.992000	10936.3310000	5468.1655000	6.2138244

1 inch = 2.539954 centimetres.
1 foot = 3.0479449 decimetres.
1 yard = 0.9143835 metre.
1 mile = 1.6093149 kilometre.

French Measures of Surface.

	In English square feet.	In English square yards = 9 square feet.	In English poles = 272.25 square feet.	In English roods = 10890 square feet.	In English acres = 43560 sq. feet.
Centiare or sq. metre,	10.764299	1.196033	0.0395383	0.0009885	0.0002471
Are or 100 sq. metres,	1076.429934	119.603326	3.9538290	0.0988457	0.0247114
Hectare or 10,000 sq. metres, ...	107642.993418	11960.332602	395.3828959	9.8845724	2.4711431

1 square inch = 6.4513669 square centimetres.
1 square foot = 9.2899683 square decimetres.
1 square yard = 0.83609715 square metre, or centiare.
1 acre = 0.40467102 hectare.

French Measures of Capacity.

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints = 34.65923 cubic inches.	In gallons = 8 pints = 277.27384 cubic inches.	In bushels = 8 gals. = 2218.19075 cubic ins.
Millilitre or cubic centimetre, . . .	0.06103	0.000035	0.00176	0.0002201	0.0000275
Centilitre or 10 cubic centimetres, . . .	0.61027	0.000353	0.01761	0.0022010	0.0002751
Decilitre or 100 cubic centimetres, . . .	6.10271	0.003532	0.17608	0.0220097	0.0027512
Litre or cub. decimetre,	61.02705	0.035317	1.76077	0.2200967	0.0275121
Decalitre or centistere,	610.27052	0.353166	17.60773	2.2009668	0.2751208
Hectolitre or decistere,	6102.70515	3.531658	176.07734	22.0096677	2.7512085
Kilolitre, or stere, or cubic metre, . . .	61027.05152	35.316581	1760.77341	220.0966767	27.5120846
Myriolitre or decastere,	610270.51519	353.165807	17607.73414	2200.9667675	275.1208459

1 cubic inch = 16.386176 cubic centimetres.
1 cubic foot = 28.315312 cubic decimetres, or litres.
1 gallon = 4.543358 litres.

French Measures of Weight.

	In English grains.	In troy ounces = 480 grains.	In avoirdupois lbs. = 7000 grains.	In cwts. = 112 lbs. = 784000 grains.	Tons = 20 cwts. = 15680000 grains.
Milligram, ...	0.01543	0.000032	0.0000022	0.0000000	0.0000000
Centigram, ...	0.15432	0.000322	0.0000220	0.0000002	0.0000000
Decigram, ...	1.54323	0.003215	0.0002205	0.0000020	0.0000001
Gram, ...	15.43235	0.032151	0.0022046	0.0000197	0.0000010
Decagram, ...	154.32349	0.321507	0.0220462	0.0001968	0.0000098
Hectogram, ...	1543.23488	3.215073	0.2204621	0.0019684	0.0000984
Kilogram, ...	15432.34880	32.150727	2.2046213	0.0196841	0.0009842
Myriogram.	154323.48800	321.507267	22.0462126	0.1968412	0.0098421

1 grain = 0.064799 gram.
1 troy oz. = 31.103496 grams.
1 lb. avoir. = 0.453593 kilogr.
1 cwt. = 50.802377 kilogrs.

Temperatures are expressed upon the Centigrade scale, where the equivalent in degrees Fahrenheit is not also given, and barometric measurements are given in millimetres.

For the ready conversion of gaseous volumes into weights, the *crith*, or standard multiple proposed by A. W. Hofmann, has been adopted in the present work. The crith is the weight of one litre or cubic decimetre of hydrogen at 0° C. and at a pressure of 760 millimetres of mercury. The following is Hofmann's description of the value and applications of this unit.

"The actual weight of this cube of hydrogen, at the standard temperature and pressure mentioned, is 0.0896 gram; a figure which I earnestly beg you to inscribe, as with a sharp graving tool, upon your memory. There is probably no figure in chemical science more important than this one to be borne in mind, and to be kept ever in readiness for use in calculation at a moment's notice. For this litre-weight of hydrogen = 0.0896 gram (I purposely repeat it) is the standard multiple, or coefficient, by means of which the weight of one litre of any other gas, simple or compound, is computed. Again, therefore, I say, do not slip this figure—0.0896 gram. So important, indeed, is this

standard weight unit, that some name—the simpler and briefer the better—is needed to denote it. For this purpose I venture to suggest the term *crith*, derived from the Greek word κριθή, signifying a barley-corn, and figuratively employed to imply a small weight. The weight of 1 litre of hydrogen being called 1 crith, the volume-weight of other gases, referred to hydrogen as a standard, may be expressed in terms of this unit.

"For example, the relative volume-weight of chlorine being 35.5, that of oxygen 16, that of nitrogen 14, the actual weight of 1 litre of each of these elementary gases, at 0° C. and $0^{m}.76$ pressure, may be called respectively 35.5 *criths*, 16 *criths*, and 14 *criths*.

"So, again, with reference to the compound gases, the relative volume-weight of each is equal to half the weight of its product-volume. Hydrochloric acid (HCl), for example, consists of 1 vol. of hydrogen + 1 vol. of chlorine = 2 volumes; or, by weight, $1 + 35.5 = 36.5$ units; whence it follows that the relative volume-weight of hydrochloric acid gas is $\frac{36.5}{2} = 18.25$ units; which last figure therefore expresses the number of *criths* which one litre of hydrochloric acid gas weighs at 0° C. temperature and $0^{m}.76$ pressure; and the crith being (as I trust you already bear in mind) 0.0896 gram, we have

$$18.25 \times 0.0896 = 1.6352$$

as the actual weight in grams of hydrochloric acid gas.

"So, once more, as the product-volume of water-gas (H_2O) (taken at the above temperature and pressure) contains 2 vols. of hydrogen + 1 vol. of oxygen, and therefore weighs $2 + 16 = 18$ units, the single volume of water-gas weighs $\frac{18}{2} = 9$ units; or, substituting as before the concrete for the abstract value, 1 litre of water-gas weighs 9 *criths;* that is to say, 9×0.0896 gram, $= 0.8064$ gram.

"In like manner the product-volume of sulphuretted hydrogen (H_2S) = 2 litres of hydrogen, weighing two criths, + 1 litre of sulphur gas, weighing 32 criths, together $2 + 32 = 34$ criths, which, divided by 2, gives $\frac{34}{2} = 17$ criths $= 17 \times 0.0896$ gram $= 1.5232$ gram = the weight of 1 litre of sulphuretted hydrogen at standard temperature and pressure.

"And so, lastly, of ammonia (NH_3), it contains in 2 litres 3 litres of hydrogen, weighing 3 criths, and 1 litre of nitrogen, weighing 14 criths; its total product volume-weight is therefore $3 + 14 = 17$ criths, and its single volume or litre-weight is consequently

$$\frac{17}{2} = 8.5 \text{ criths} = 8.5 \times 0.0896 \text{ gram} = 0.7616 \text{ gram}.$$

"Thus, by the aid of the hydrogen-litre-weight or crith = 0.0896 gram, employed as a common multiple, the actual or concrete weight of 1 litre of any gas, simple or compound, at standard temperature and pressure, may be deduced from the mere abstract figure expressing its volume-weight relatively to hydrogen."

The number expressing in criths the weight of 1 litre of any gas or vapor being identical with its specific gravity compared with hydrogen

taken as unity, it is easy, when this number is known, to calculate the specific gravity of the gas compared with air taken as unity. For this purpose it is only necessary to multiply by .0693, which is the specific gravity of hydrogen compared with air = 1.

Thus the specific gravity of oxygen compared with air is

$$16 \times .0693 = 1.1088;$$

of chlorine,

$$35.5 \times .0693 = 2.46015;$$

of hydrochloric acid,

$$18.25 \times .0693 = 1.264725.$$

NON-METALS.

CHAPTER XXII.

MONAD ELEMENTS.

SECTION I.

HYDROGEN, H_2.

Atomic weight = 1. *Molecular weight* = 2. *Molecular volume* $\square\square$. 1 *litre weighs* 1 *crith. Atomicity* ′, *being the standard of comparison. Liquefies at* —140° C. (—220° F.) *under a pressure of* 650 *atmospheres.*

History.—Paracelsus, in the sixteenth century, first noticed that when iron is dissolved in sulphuric acid a gas is evolved, which he, however, assumed to be air. Hydrogen was first thoroughly investigated by Cavendish in 1766, who gave to it the name of *inflammable air.*

Occurrence.—In the free state, hydrogen occurs in the gases of volcanoes (Bunsen). It is also evolved in small quantities during the fermentation and spontaneous decomposition of animal and vegetable matters, and is therefore present in the intestinal gases of some animals, and in the gases which issue from petroleum springs. It occurs inclosed in the carnallite of the Stassfurt potash mines, where it appears to have been formed by the action of ferrous chloride upon water in absence of air:

$$\underset{\text{Ferrous chloride.}}{6\mathbf{Fe}Cl_2} + \underset{\text{Water.}}{6\mathbf{O}H_2} = \underset{\text{Ferric chloride.}}{2\mathbf{Fe}_2Cl_6} + \underset{\text{Ferric hydrate.}}{\mathbf{Fe}_2Ho_6} + 3H_2.$$

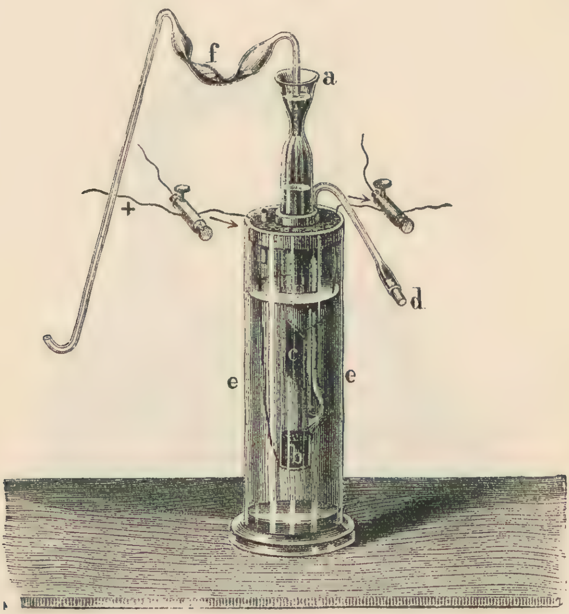
It has been found occluded in meteoric iron (Graham). Spectroscopic observation shows that free hydrogen exists in the sun, in certain stars, and in nebulæ, the temperature of these bodies being too high to permit of the union of the hydrogen with other elements.

In combination, hydrogen occurs in enormous quantities in nature. Water contains hydrogen (one-ninth of its weight), and from this fact the name *hydrogen* (from ὕδωρ, water; and γεννάω, I bring forth) is derived. In small quantities it occurs combined with nitrogen as ammonia in the air; whilst with sulphur, as sulphuretted hydrogen, and with chlorine, as hydrochloric acid, it is found in mineral and volcanic

springs. It is an important constituent of nearly all animal and vegetable substances, and occurs in many minerals.

Preparation.—1. Hydrogen is obtained in a state of purity by the electrolysis of acidulated water (see *Electrolysis*). The most convenient apparatus for this purpose is that devised by Bunsen (Fig. 14). The internal vessel *ab*, is filled up to the bend of the tube *d* with dilute sulphuric acid (1 volume of chemically pure sulphuric acid to 10 volumes of water). The positive electrode *b* consists of an amalgam of mercury and zinc, which is not attacked by the acid except when the current is passing. A platinum plate, *c*, forms the negative electrode. The connecting wires are fused through the glass. The whole is inclosed in an outer vessel, *ee*, filled with alcohol to prevent the wires from being

FIG. 14.



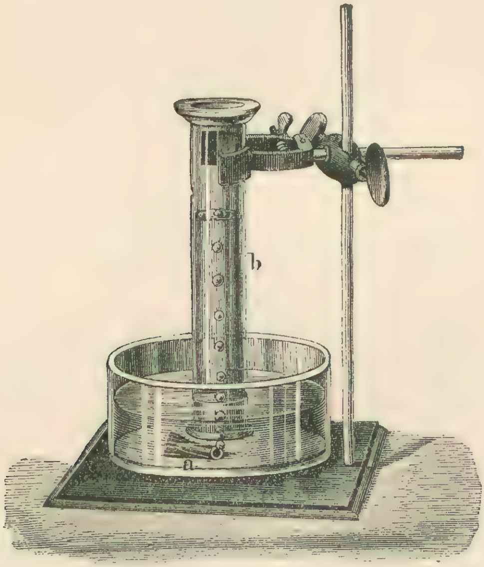
heated by the passage of the current, which is generated by two or three Bunsen's or Grove's cells. The oxygen which would otherwise be given off at *b*, combines with the zinc to form zincic oxide, which dissolves in the sulphuric acid. A stream of pure hydrogen is evolved at *c*, and is dried by passing through concentrated sulphuric acid contained in the bulbs *f*. A concentrated solution of zincic sulphate collects over the positive electrode, but this may be removed by pouring in fresh liquid at *a*, which will cause the saturated solution to flow off at *d*.

2. Potassium and sodium decompose water at ordinary temperatures with evolution of hydrogen—

$$\underset{\text{Water.}}{2OH_2} + Na_2 = \underset{\text{Sodic hydrate.}}{2ONaH} + H_2.$$

In the case of potassium, the action takes place with such violence and evolution of heat as to ignite the hydrogen. The safest mode of performing the experiment with sodium is to inclose the metal in a short piece of lead tubing, *a* (Fig. 15), $\frac{3}{16}$ inch in diameter, hammered together at one end. The sodium is tightly rammed into the tube, which is then thrown into water. The weight of the lead causes the sodium, which is specifically lighter than water, to sink. The gas is steadily evolved from the open end of the tube, and may be collected in an inverted glass cylinder *b*, previously filled with water. The usual method of performing the experiment, by throwing the sodium

FIG. 15.



on water and pressing it under the mouth of the inverted cylinder by means of a small net of wire gauze, is not unattended with danger, owing to the escape of globules of sodium through the meshes of the gauze; for when sodium decomposes water in a confined space, it sometimes occasions a violent explosion.

3. Very pure hydrogen may be obtained by dissolving magnesium in dilute sulphuric acid. The method of applying this reaction is the same as that described in the following paragraph.

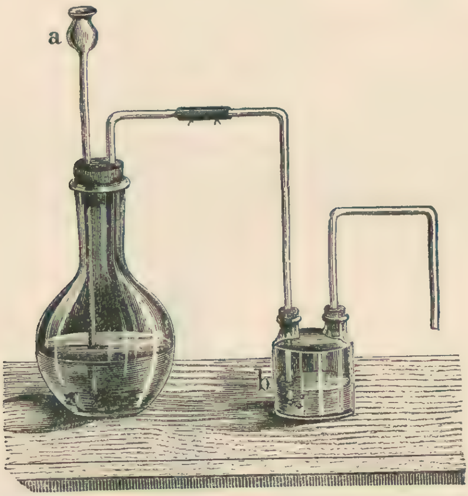
4. Hydrogen is most conveniently prepared for laboratory purposes by acting on zinc with sulphuric acid—

$$\underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} + Zn = \underset{\text{Zincic sulphate.}}{\mathbf{S}O_2Zno''} + H_2.$$

The zinc is previously granulated by melting it and pouring it into water. The sulphuric acid, diluted with six or seven times its weight

of water, is poured through the funnel tube *a* (Fig. 16) upon the zinc contained in the flask. The gas is washed by allowing it to bubble through the water in the Woulff's bottle *b*, and may be collected in cylinders or bell-jars over the pneumatic trough. In this and in all other methods of preparing hydrogen, it is necessary, if the gas is to be inflamed, to be perfectly certain that all air has first been expelled from the apparatus by the evolved gas. This is best ascertained by collecting a small quantity in a test-tube over water and igniting it, the tube being held mouth downwards. If the gas burns quietly, the air has been sufficiently expelled; if it takes fire with a slight explosion, the evolution of gas must be continued. Neglect of these precautions may lead to very dangerous explosions. Hydrogen prepared by this method

FIG. 16.



is apt to be contaminated with the following impurities: arseniuretted hydrogen, if the zinc or sulphuric acid contains arsenic; nitrous and nitric oxides, if nitric acid is present in the sulphuric acid; phosphoretted hydrogen, if the zinc contains phosphorus; sulphuretted hydrogen or sulphuric anhydride, if hot acid be added to the zinc. These impurities impart an unpleasant odor to the gas. In order to remove them, Dumas passes the gas through two **U**-tubes, filled with broken glass, which is moistened in the first tube with plumbic nitrate, to absorb sulphuretted hydrogen, and in the second with argentic sulphate, to absorb arseniuretted and phosphoretted hydrogen. The gas then passes through a third **U**-tube filled with pumice moistened with strong caustic potash; and then, in order to dry it thoroughly, first through a tube containing calcic chloride, and afterwards through one filled with phosphoric anhydride.* Hydrogen, no matter how prepared, is apt to

* The use of concentrated sulphuric acid as a desiccating agent ought to be avoided, if a very pure gas is required, as hydrogen slowly reduces this acid in the cold with formation of sulphurous anhydride.

contain traces of nitrogen, derived in part from nitrogen dissolved in the liquids employed, but chiefly introduced by diffusion through the joints of the apparatus. There is no method known of removing this nitrogen. Oxygen, when present in traces, may be got rid of by leaving the gas in contact with spongy platinum, which causes the hydrogen and oxygen to combine to form water. If the oxygen were present in large quantities, the introduction of spongy platinum would occasion an explosion.

Hydrochloric acid diluted with twice its weight of water may be substituted for dilute sulphuric acid in the above mode of preparation—

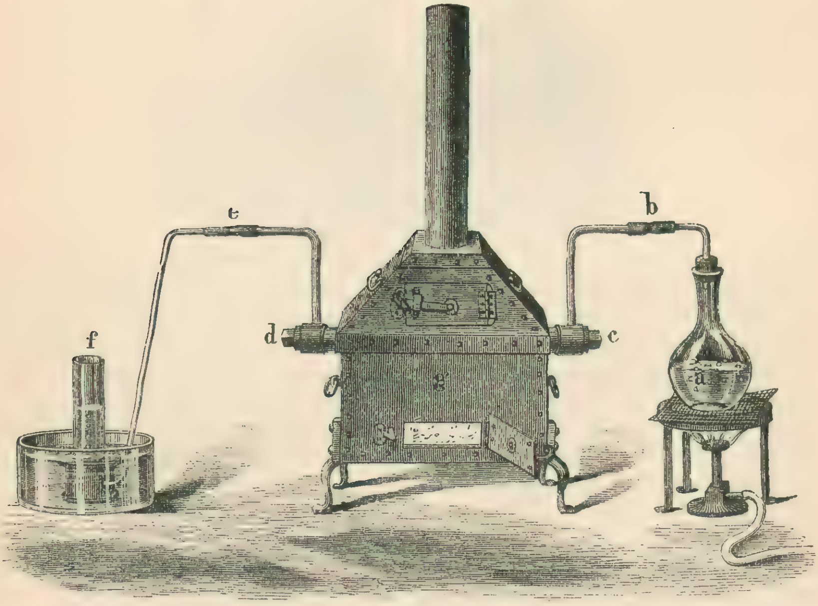
$$\underset{\text{Hydrochloric acid.}}{2HCl} + Zn = \underset{\text{Zincic chloride.}}{ZnCl_2} + H_2.$$

Iron may also be substituted for zinc—

$$\underset{\text{Sulphuric acid.}}{SO_2Ho_2} + Fe = \underset{\text{Ferrous sulphate.}}{SO_2Feo''} + H_2;$$

but in this case the gas has an unpleasant odor, occasioned by the presence of volatile hydrocarbons which are formed from the carbon contained in the iron. These may be absorbed by charcoal.

FIG. 17.



5. When hydrogen is required in very large quantities for manufacturing or other purposes, it is best prepared by passing steam over iron turnings or wire contained in an iron tube, and heated to redness in a furnace (Fig. 17). The iron combines with the oxygen of the water

to form triferric tetroxide (magnetic oxide of iron), whilst hydrogen is liberated.

$$3Fe + 4OH_2 = {}^{iv}(\mathbf{Fe}_3)^{viii}O_4 + 4H_2.$$

Water. Triferric tetroxide.

The tube *b c d e* is of iron, and the wider portion, which contains the turnings, is closed at *c* and *d* by iron screws. The steam is generated in the flask *a*, and the hydrogen is collected in the cylinder *f* at the pneumatic trough.

Charcoal may be substituted for iron turnings in the foregoing experiment; but in this case it is necessary to pass the gas through slaked lime to absorb the carbonic anhydride which is formed at the same time:

$$C + 2OH_2 = CO_2 + 2H_2.$$

Water. Carbonic anhydride.

If, however, the temperature be raised too high, carbonic oxide will be formed; and this gas cannot be removed from the hydrogen by any process practicable on a large scale. It is very difficult, if not impossible, to obtain hydrogen free from carbonic oxide by this process.

Further Modes of Formation.—1. When sodium is heated in gaseous hydrochloric acid, it combines with the chlorine, liberating hydrogen:

$$2HCl + Na_2 = 2NaCl + H_2.$$

Hydrochloric acid. Sodic chloride.

2. When zinc is heated with a solution of potassic hydrate, preferably in contact with iron, hydrogen is evolved. The zinc displaces the hydrogen of the potassic hydrate:

$$2OKH + Zn = ZnKo_2 + H_2.$$

Potassic hydrate. Potassic zinc oxide.

3. The aqueous solutions of the salts of ammonia, with the exception of the nitrate, when acted upon with zinc, evolve hydrogen. The gas is given off even at ordinary temperatures, but the evolution is more rapid at 40° C. (104° F.). With a mixture of zinc and iron, and a solution of an ammonium salt containing free ammonia, hydrogen is evolved as rapidly as from zinc and dilute sulphuric acid (Lorin).

4. On heating formates or oxalates with an excess of a caustic alkali, hydrogen is given off:

$$CHOKo + HKo = COKo_2 + H_2.$$

Potassic formate. Potassic hydrate. Potassic carbonate.

$$\left\{\begin{matrix} COKo \\ COKo \end{matrix}\right. + 2HKo = 2COKo_2 + H_2.$$

Potassic oxalate. Potassic hydrate. Potassic carbonate.

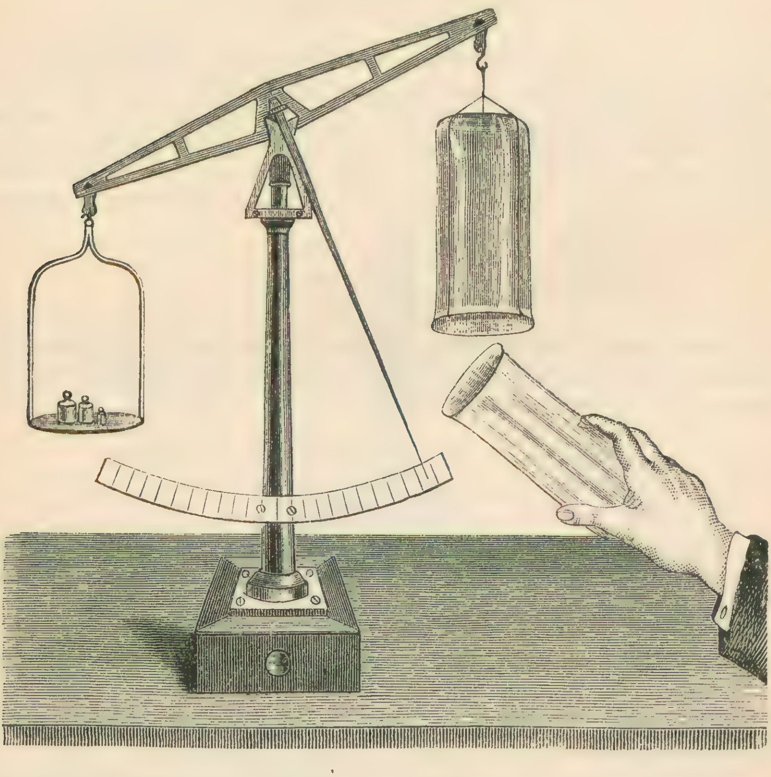
Salts of several other organic acids also evolve hydrogen under the same conditions.

5. By the action of intense heat, such as that of the electric spark, upon steam, the latter is decomposed into its elements, oxygen and hydrogen.

6. In the destructive distillation of many organic substances containing hydrogen, this gas is evolved, partly in the free state and partly in the form of hydrocarbons and other organic compounds. It is therefore found in large quantities in illuminating gas, which is obtained by the destructive distillation of coal, oil, or resin.

Properties.—Hydrogen is a colorless gas, devoid of taste and smell, about fourteen and a half times lighter than air. Its specific gravity is 0.0693 (air = 1). Owing to its lightness, it may be collected in

FIG. 18.

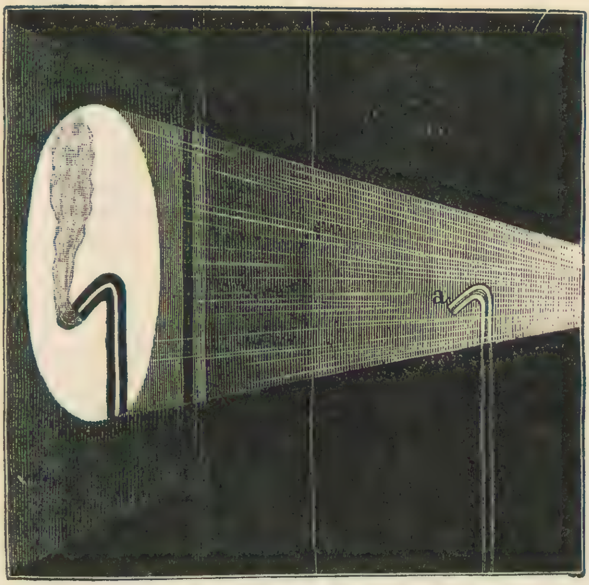


inverted vessels by upward displacement, and may be retained in such vessels, even when these are open, for some time; but if the vessels be turned mouth upwards the gas will escape in a few seconds. The experiment of pouring hydrogen *upwards* from one vessel into another may be shown by the following arrangement. An inverted beaker (Fig. 18) is suspended from one of the arms of a moderately delicate balance, and is accurately counterpoised. On pouring hydrogen upwards

into the beaker, as seen in the figure, the arm of the balance from which the beaker is suspended will rise.

The lightness of hydrogen may also be demonstrated by the following experiment. A delivery-jet, *a* (Fig. 19), bent downwards, is placed in the path of the rays of an electric lamp, so as to cast a clear image on

Fig. 19.



the screen. As soon as hydrogen is allowed to pass through the jet, the upward movement of the gas will be visible on the screen in the shape of a succession of streaks and shadows rushing upwards from the jet, denoting the passage of a medium possessing a refractive power different from that of the surrounding air.

Owing to its lightness, hydrogen may be used for filling balloons. Soap-bubbles filled with the gas rise rapidly through the air.

Hydrogen cannot support animal life. Small animals placed in a vessel of the gas die speedily. This effect is not due to any specifically poisonous action of the gas, but simply to the exclusion of oxygen, which is essential to life. If mixed with air, it may be breathed for some time, and, as long as it is contained in the lungs, imparts to the voice a peculiar squeaking tone.

Hydrogen is very inflammable. It burns in air with a pale blue flame, which is intensely hot, but emits scarcely any light. Mixed with suitable proportions of air or oxygen it explodes violently in contact with flame.

Hydrogen is only slightly soluble in water. Its solubility is the same for all temperatures between 0° and 20° C. (32°–68° F.), at which temperatures water dissolves about one-fiftieth of its volume of the gas.

Platinum and iron at a red heat are permeable to hydrogen gas.

But the metal which possesses this property in the highest degree, and permits the passage of hydrogen at temperatures far below redness, is, as has been shown by Graham, palladium. This action is connected with the property which these metals possess of absorbing hydrogen when heated and retaining it when cold, a property which was termed by Graham *occlusion.* The absorptive power of a metal for hydrogen may be determined by the following method: The weighed metal, for example palladium, is introduced into a glazed porcelain tube, to which a Sprengel pump is attached. In this pump, by the fall of mercury down a long tube, a more perfect vacuum is produced than can be obtained by other means. The porcelain tube is exhausted, and heated to redness. Hydrogen is then admitted and passed over the metal for a considerable time, after which the metal is allowed to cool in the gas. The tube is then exhausted a second time and heat again applied, when the hydrogen which has been occluded will be evolved at the reduced pressure, and may be pumped off and collected in a measuring-tube at the bottom of the fall-tube of the pump. In this way Graham found that palladium at a red heat occludes more than 900 times its volume of hydrogen. Even at ordinary temperatures this metal can occlude no less than 376 times its volume of the gas. The hydrogen thus absorbed assumes the solid state, and forms a true alloy with palladium. To hydrogen in this condition Graham applied the name *hydrogenium,* in order to denote its metallic character. The density, tenacity, and electric conductivity of the alloy are less than those of pure palladium.

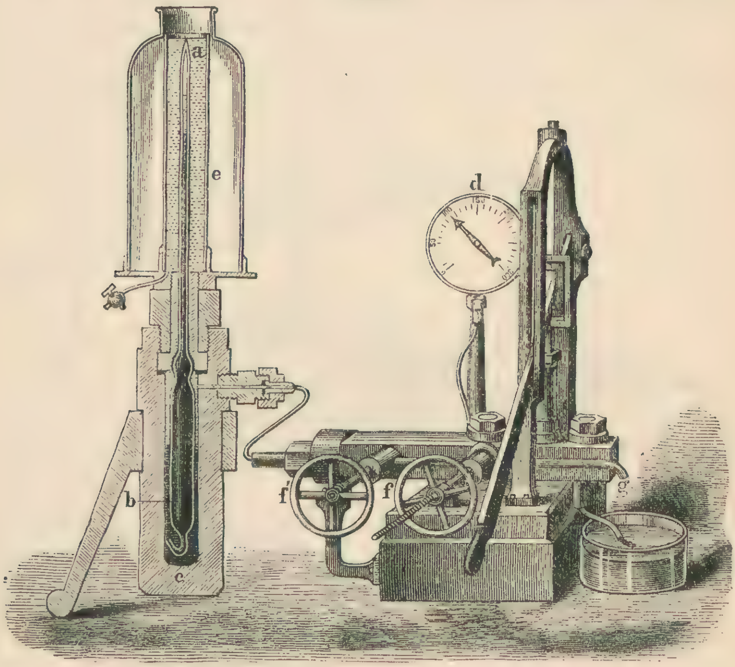
In examining, by means of the Sprengel vacuum, the meteoric iron of Lenarto (containing 90.88 p. c. iron, 8.45 nickel, and 0.66 cobalt), Graham found that this metallic substance yielded, when heated to redness, 2.85 times its volume of a gas containing 85.68 per cent. of hydrogen. As red-hot iron at ordinary atmospheric pressure does not absorb more than half its own volume of hydrogen, the above observation would seem to suggest that this meteorite had, during some period of its existence, been exposed to hydrogen of greater pressure than the atmosphere of our earth. Spectroscopic observation points to the presence of atmospheres of hydrogen in the sun and fixed stars.

Hydrogen was liquefied for the first time in 1877 by Pictet and Cailletet, who achieved this triumph of experimental skill independently and almost simultaneously. The difference between the two methods consisted chiefly in the means of refrigeration employed. Pictet employed only external, Cailletet chiefly internal, refrigeration. In the first case, the cooling is produced by means of ordinary refrigerants; in the second, it depends on the fact that a gas, if permitted to expand suddenly, undergoes a great depression of temperature. The latter phenomenon may be shown first by saturating the air under the receiver of an air-pump with moisture and then exhausting. At each stroke of the pump the receiver will fill with fog, owing to the condensation of the aqueous vapor by the cold produced.

Cailletet's apparatus is represented in Fig. 20. The tube *ab*, shown separately in Fig. 21, is filled with *perfectly dry* hydrogen, and its lower extremity is then plunged under the mercury contained in the strong wrought-iron reservoir *c*, represented in section in the figure.

After the tube has been firmly screwed into its place, a freezing mixture is introduced into the cylinder *e* and the hydraulic pump represented to the right of the figure is put in action. The water which is thus forced into the reservoir *c*, presses on the surface of the mercury, causing it to rise within the tube *a*, and thus to compress the gas powerfully. In this way a pressure of 200 atmospheres is obtained, which

Fig. 20.



is registered by the manometer *d*. In order to compress the gas still further, a steel plunger, worked by the wheel *f*, is employed, and by this means the pressure may be increased to 300 atmospheres. As soon as this pressure is reached the gas is allowed to expand suddenly. This is accomplished by means of a screw worked by the wheel *f′*, the unscrew-

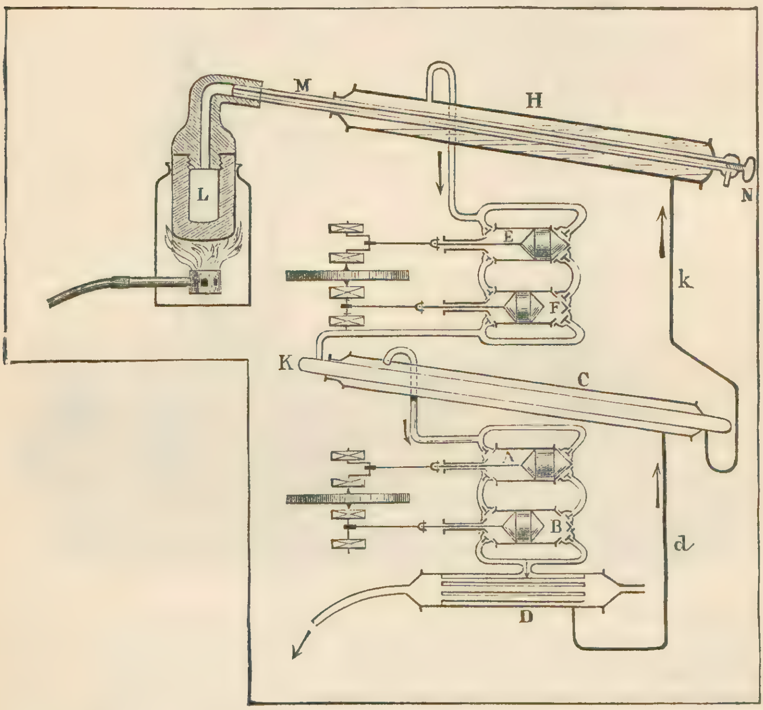
Fig. 21.

ing of which permits the water to flow out of the reservoir at *g*. At the moment of expansion the tube containing the hydrogen becomes filled with fog, showing that the gas has condensed to minute particles of liquid. Most gases can be obtained in a coherent liquid state by means of this apparatus, but in the case of hydrogen and some of the other

less coercible gases the phenomenon can be shown only by the production of a fog. This, however, is sufficient to prove the fact of liquefaction; for the moment a colorless gas loses its transparency it ceases to be a gas.

Pictet's apparatus is much more complicated. The outer casing of the condenser *C* (Fig. 22) is filled with liquid sulphurous anhydride. By means of the double pump *AB*, which possesses cylinders of the capacity of 3 litres each, and is worked by a steam-engine at the rate of 100 strokes per minute, the gaseous sulphurous anhydride is pumped

FIG. 22.



off from the condenser as quickly as it is vaporized. By this rapid evaporation the temperature of the condenser is kept as low as —65° C. (—85° F.). The gaseous sulphurous anhydride drawn off by the pump passes into a second condenser *D*, cooled by a current of water. Here it again liquefies under pressure, and is returned by the tube *d* to the first condenser, so that a constant circulation of sulphurous anhydride is kept up in the direction of the arrows. The outer case of a third condenser, *H*, is filled with liquid carbonic anhydride, which boils off under the action of the pumps *EF*, producing a refrigeration of —140°. The gaseous carbonic anhydride passes from the pumps into the inner tube *K* of the condenser *C*, where it is liquefied under a pressure of 5 atmospheres by the cold produced by the evaporation of the sulphurous anhydride. It is then returned in the liquid state by the tube *k* to *H*,

so that a circulation of carbonic anhydride is kept up. The hydrogen to be liquefied is generated by the action of heat on a mixture of perfectly dry potassic hydrate and potassic formate contained in a strong wrought-iron retort *L*. It passes into the very strong glass tube *M*, where it is liquefied at a pressure of 650 atmospheres by the cold produced by the evaporation of the liquid carbonic anhydride. On suddenly opening the stopcock *N*, the hydrogen escapes with enormous violence in the form of a liquid jet, and, if present in any considerable quantity, solidifies by the rapidity of its own evaporation, the solid particles striking against the ground with a sound as of small shot. It has been found quite impossible to collect the solid or liquid hydrogen when it has once escaped from the tube.

Since the above results were obtained, Wroblewski and Olzewski have successfully employed in the liquefaction of gases the intense cold produced by the evaporation of liquid ethylene *in vacuo*.

SECTION II.

CHLORINE, Cl_2.

Atomic weight = 35.5. *Molecular weight* = 71. *Molecular volume* □□. 1 *litre weighs* 35.5 *criths*. *Has not been solidified*. *Liquefies at* 15.5° C. (59.9° F.) *under a pressure of* 4 *atmospheres*. *Atomicity* $'$. *Evidence of atomicity*, HCl.

History.—Chlorine was discovered by Scheele in 1774. Berthollet (1785) supposed it to be a compound of hydrochloric acid with oxygen, a view held till 1809, when Gay-Lussac and Thenard suggested that it might be regarded as an element. Davy in 1810 declared in favor of the latter view, and contributed greatly to its general acceptance by chemists.

Preparation.—1. Chlorine is most conveniently prepared by gently heating a mixture of manganic peroxide and hydrochloric acid. The reaction takes place in two stages:

a.	MnO_2	+	$4HCl$	=	$MnCl_4$	+	$2OH_2$.
	Manganic peroxide.		Hydrochloric acid.		Manganic perchloride.		Water.

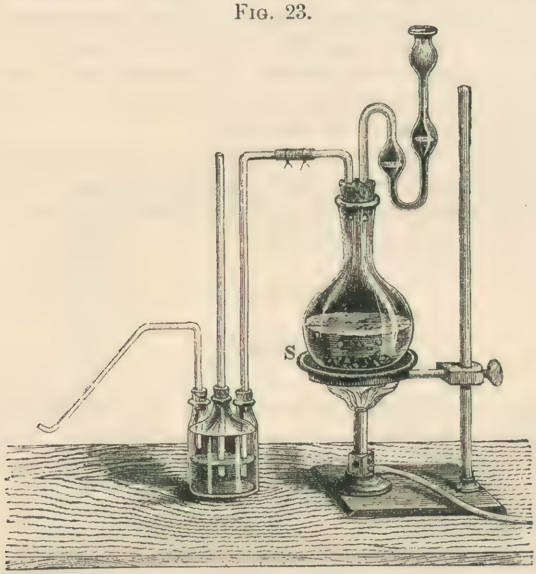
b.	$MnCl_4$	=	$MnCl_2$	+	Cl_2
	Manganic perchloride.		Manganous chloride.		Chlorine.

The chlorine should be generated in a large flask (Fig. 23) heated over a sand-bath *S*, and may be washed by passing it through water, in order to absorb hydrochloric acid. If required dry, it should pass through a second wash-bottle containing concentrated sulphuric acid. Owing to its great specific gravity, it may be collected by downward displacement. If it is desired to collect it at the pneumatic trough, the water must be warmed, as cold water absorbs the gas rapidly. Mercury

cannot be employed in collecting the gas, as it is instantly attacked by chlorine.

When a larger quantity of chlorine is required for laboratory purposes, the generating flask may be replaced by a large leaden Woulff's bottle heated in a steam jacket. Into this bottle a charge of a quarter of a hundred-weight of manganic peroxide may be introduced at once.

FIG. 23.



2. The hydrochloric acid required for the preparation of chlorine may be formed in the course of the reaction. Thus, by heating a mixture of sulphuric acid, sodic chloride, and manganic peroxide, chlorine is liberated:

$$\underset{\text{Manganic peroxide.}}{\mathbf{Mn}O_2} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2} + \underset{\text{Sodic chloride.}}{2NaCl} = \underset{\text{Sodic sulphate.}}{\mathbf{S}O_2Nao_2} +$$

$$\underset{\text{Manganous sulphate.}}{\mathbf{S}O_2Mno''} + \underset{\text{Water.}}{2\mathbf{O}H_2} + Cl_2.$$

The sulphuric acid acts on the sodic chloride, producing hydrochloric acid, which in its turn acts on the manganic peroxide as in 1. In this reaction all the chlorine present is evolved.

If in process 1 a mixture of manganic peroxide, hydrochloric acid, and sulphuric acid be employed, the whole of the chlorine will also be liberated:

$$\underset{\text{Manganic peroxide.}}{\mathbf{Mn}O_2} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Manganous sulphate.}}{\mathbf{S}O_2Mno''} + \underset{\text{Water.}}{2\mathbf{O}H_2} + Cl_2.$$

Other peroxides and oxidizing agents may be substituted for the manganic peroxide in process 1. In this way plumbic peroxide, baric peroxide, or potassic dichromate, may be employed. Any oxide will yield chlorine with hydrochloric acid, provided that the corresponding chloride either does not exist, or is unstable at the temperature employed. With potassic dichromate the reaction is as follows:

$$\underset{\text{Potassic dichromate.}}{\left\{\begin{matrix}\mathbf{Cr}O_2Ko \\ O \\ \mathbf{Cr}O_2Ko\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{14HCl} = \underset{\text{Potassic chloride.}}{2KCl} + \underset{\text{Chromic chloride.}}{{'\mathbf{Cr}'''}_2Cl_6} + \underset{\text{Water.}}{7\mathbf{O}H_2} + 3Cl_2.$$

When required on a very large scale for manufacturing purposes, as for example in the production of bleaching powder, chlorine is frequently prepared by reaction (1) from hydrochloric acid and manganic peroxide. The mixture is contained in large tanks made of Yorkshire flagstones fastened together with iron clamps, and made tight by means of vulcanized caoutchouc. The tanks are inclosed in an outer casing through which steam passes.

3. When gaseous hydrochloric acid mixed with air is passed through a red-hot tube charged with fragments of brick to increase the heating surface, the hydrogen of a portion of the hydrochloric acid combines with the oxygen of the air to form water, and chlorine is liberated. By passing the gaseous products through water, the undecomposed hydrochloric acid is absorbed, and a mixture of chlorine with nitrogen and oxygen is obtained. If the fragments of brick are impregnated with cupric sulphate, the reaction takes place much more thoroughly, and the greater part of the hydrochloric acid yields its chlorine in the free state. This latter process is now employed in the manufacture of bleaching powder. The cupric sulphate remains apparently unaltered during the reaction, and requires but seldom to be renewed. Cuprous chloride may be substituted for cupric sulphate. Actions of this class, in which the mere presence of a substance appears to determine chemical change in other bodies, the substance itself remaining apparently unchanged, are termed *catalytic*. The final reaction in the above cases is expressed by the following equation:

$$\underset{\text{Hydrochloric acid.}}{4HCl} + O_2 = \underset{\text{Water.}}{2\mathbf{O}H_2} + 2Cl_2.$$

But it is more probable that, in the case of the cuprous chloride, the reaction takes place in two stages, cupric chloride being continually formed and immediately afterwards decomposed:

$$(a.)\quad \underset{\text{Cuprous chloride.}}{{'\mathbf{Cu}'}_2Cl_2} + \underset{\text{Hydrochloric acid.}}{2HCl} + O = \underset{\text{Cupric chloride.}}{2\mathbf{Cu}Cl_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

$$(b.)\quad \underset{\text{Cupric chloride.}}{2\mathbf{Cu}Cl_2} = \underset{\text{Cuprous chloride.}}{{'\mathbf{Cu}'}_2Cl_2} + Cl_2.$$

In fact, when cuprous chloride, moistened with hydrochloric acid, is heated in air, cupric chloride is formed according to equation (*a*). On raising the temperature, chlorine is evolved and cuprous chloride again produced according to (*b*). In the process just described these reactions follow each other so closely as to present the appearance of a single continuous action.

It is probable that all so-called catalytic actions depend in like manner upon the formation of some unstable intermediate compound, which, being decomposed as fast as it is formed, escapes observation.

Platinum black, and finely divided chromic oxide, exhibit when heated a similar catalytic action on a mixture of hydrochloric acid and air.

4. Certain metallic chlorides, as auric and platinic chlorides, evolve the whole of their chlorine when heated:

$$\underset{\text{Platinic chloride.}}{PtCl_4} = Pt + 2Cl_2.$$

5. When strong aqueous hydrochloric acid is submitted to electrolysis with carbon electrodes, it is decomposed into its elemeants, hydrogen being evolved at the negative and chlorine at the positive electrode.

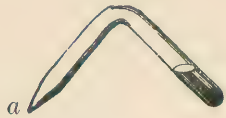
Properties.—Chlorine is a greenish-yellow gas. Its name, from χλωρός, greenish-yellow, is derived from this property. It is uninflammable in air, and possesses a powerfully irritating odor, even when greatly diluted with air. It is one of the heaviest among substances that are gaseous at ordinary temperatures, being 2.44 times heavier than air. The vapor-density of pure chlorine determined under ordinary pressures is constant up to 1600°, and corresponds with the molecular formula Cl_2. If, however, the chlorine be mixed with air in order to diminish the pressure of the chlorine, the vapor-density will show a gradual diminution as the temperature rises—a diminution amounting at 1600° to about 16 per cent. This diminution is due to a partial dissociation of the molecules of the gas into single atoms. This dissociation, which in the case of chlorine is incomplete at the highest temperatures which can be commanded in such determinations, extends further in the case of bromine and, in the case of iodine vapor diluted with air, is complete at 1400° (see *Bromine* and *Iodine*).

Water at 20° C. (68° F.) dissolves about twice its volume of chlorine, the solution possessing the color and odor of the gas. The solubility decreases rapidly as the temperature rises. If the water be cooled with ice while chlorine is passed into it, a crystalline compound of chlorine and water of the formula $Cl_2 10OH_2$ is formed.

When exposed to the air, even at low temperatures, these crystals rapidly give off chlorine and melt; but if pressed quickly between cold filtering-paper and sealed up in a glass tube, they do not decompose till the temperature rises to 38° C. (100° F.), when the chlorine which they evolve is liquefied by its own pressure, and forms a layer of liquid chlorine under the layer of saturated chlorine water in the tube. If the tube be bent at an obtuse angle as in Fig. 24, and the empty limb *a* be plunged into a freezing mixture, the liquid chlorine will distil

over and condense in *a*. This was the method originally employed by Faraday in the liquefaction of chlorine.

FIG. 24.



Chlorine water is a powerful oxidizing agent: thus it instantaneously converts sulphurous acid into sulphuric acid. In this reaction the chlorine combines with the hydrogen of the water, and the oxygen which is thus set at liberty acts in the nascent state on the sulphurous acid:

$$\underset{\text{Sulphurous acid.}}{SOHo_2} + Cl_2 + \underset{\text{Water.}}{OH_2} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + 2HCl.$$

Chlorine water may be preserved for a considerable time, if kept in a well-stoppered bottle and in a dark place. Under the influence of light the chlorine combines with the hydrogen of the water, as above, and oxygen is evolved.

Chlorine has very powerful affinities. It combines directly with hydrogen to form hydrochloric acid. When mixed in equal volumes and exposed to direct sunlight, hydrogen and chlorine combine with explosion.

Chlorine removes hydrogen from its compounds with carbon. When a rag moistened with turpentine is plunged into a jar of chlorine, the chlorine and hydrogen unite, with evolution of heat and light, whilst carbon is liberated.

$$\underset{\text{Turpentine.}}{C_{10}H_{16}} + 8Cl_2 = \underset{\text{Hydrochloric acid.}}{16HCl} + 10C.$$

The same phenomenon is exhibited when a burning taper is introduced into a jar of chlorine; the hydrogen of the taper continues to burn, but the carbon separates out, forming dense clouds of soot.

By a more moderate action, chlorine may be made to displace hydrogen in compounds of carbon with hydrogen, a process known as *substitution*. Thus when equal volumes of marsh-gas and chlorine are exposed to diffused daylight, methylic chloride and hydrochloric acid are formed:

$$\underset{\text{Marsh-gas.}}{CH_4} + Cl_2 = \underset{\substack{\text{Methylic}\\\text{chloride.}}}{CH_3Cl} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl.}$$

Moist chlorine combines directly at ordinary temperatures with all the metals, except iridium, and with most of the metalloids. It has not been made to combine directly with carbon. Many of the elements,

such as phosphorus and finely divided arsenic, antimony, and copper, inflame when introduced into the gas, owing to the heat evolved in combination.

Chlorine is employed to bleach linen and cotton fibre, and to destroy vegetable coloring matters. (On the mode of its employment for this and similar purposes see *Bleaching Powder.*) The action takes place in presence of water, and is an oxidizing action as already described. Dry chlorine does not bleach. When chlorine water is added to a solution of indigo, the blue color disappears. Chlorine has no action on most mineral colors, or on printing and China inks, in which the black substance is finely divided carbon. Black writing ink, however, which is the iron salt of an organic acid, is at once bleached by it. This difference may be shown by obliterating a printed page with writing ink and then dipping it into chlorine water, when the printed characters will reappear.

Chlorine is also employed as a disinfectant, as it possesses the property of destroying putrefactive organisms, miasmata, and noxious vapors—the products of decomposition of organic matter.

Chlorine is a powerful poison. Inhaled in a diluted condition it provokes coughing; in larger quantities it produces spitting of blood, and, when concentrated, immediate death.

HYDROCHLORIC ACID, *Chlorhydric Acid, Muriatic Acid.* HCL.

Molecular weight = 36.5. *Molecular volume* $\square\square$. 1 *litre weighs* 18.25 *criths. Has not been solidified. Condenses at* 10° C. (50° F.) *under a pressure of* 40 *atmospheres.*

History.—The aqueous solution of hydrochloric acid has been known from very early times. The gas itself was discovered by Priestley in 1772, who was enabled to collect it by means of his mercurial pneumatic trough.

Occurrence.—Hydrochloric acid is given off in large quantities from active volcanoes. Some rivers which take their rise in the Andes contain from 0.1 to 0.2 per cent. of hydrochloric acid.

Preparation.—1. Hydrochloric acid gas is formed by the direct union of its elements, as described under chlorine. This experiment may be shown by means of the following arrangement. Two stoppered glass vessels of exactly equal capacity (Fig. 25) are united by a tube which may be closed by a stopcock. After closing the stopcock, one of these is filled with chlorine and the other with hydrogen, and the stoppers are replaced. On opening the stopcock in the dark, diffusion will cause the gases to mix, an action which will be more rapid if the part of the apparatus containing the chlorine be placed uppermost. If the apparatus be now exposed to the diffused light of a well-lighted room (but not to direct sunlight, otherwise an explosion will occur) the color of the diluted chlorine,

at first visible, will rapidly disappear. The reaction may be completed by exposure to sunlight for a few minutes, there being no longer any danger of explosion. If one of the stoppers be now removed under mercury, there will be no rise of the mercury in the vessel, showing that no contraction has occurred during combination and also that no free chlorine remains. If water colored blue with litmus be poured on the surface of the mercury, and the apparatus be raised until its orifice is above the mercury, but under the water, the latter will rush in, completely filling the double vessel (a proof that no free hydrogen remains), whilst the blue tint turns to red owing to the action of the acid. Equal volumes of hydrogen and chlorine therefore combine without change of volume to form hydrochloric acid gas.

Fig. 25.

2. For laboratory purposes hydrochloric acid is best prepared by the action of sulphuric acid on common salt. The salt (1 part) is contained in a large flask, and the sulphuric acid (2 parts) previously diluted with a very small quantity of water, is poured in gradually through a funnel tube reaching to the bottom of the flask, as in the apparatus for the preparation of hydrogen (Fig. 16, page 143). A rapid disengagement of gas takes place. Towards the end of the process the reaction may be aided by the application of a gentle heat.

$$\mathbf{S}O_2Ho_2 + NaCl = \mathbf{S}O_2HoNao + HCl.$$

Sulphuric acid.	Sodic chloride.	Hydric sodic sulphate.	Hydrochloric acid.

If only half of the above quantity of sulphuric acid be employed without adding water, the decomposition occurs according to the equation:

$$\mathbf{S}O_2Ho_2 + 2NaCl = \mathbf{S}O_2Nao_2 + 2HCl.$$

Sulphuric acid.	Sodic chloride.	Sodic sulphate.	Hydrochloric acid.

and the normal sulphate is formed; but, in this case, a much higher temperature is required to expel the whole of the hydrochloric acid.

The gas must be collected by downward displacement, or over mercury, as it is instantaneously absorbed by water. If, however, the aqueous solution is required, the gas may be passed at once into water.

(For the preparation of hydrochloric acid on the manufacturing scale, see *Sodic Sulphate.*)

Properties.—Pure hydrochloric acid is a colorless gas, of a sharp and suffocating odor. It does not support combustion. Its specific gravity is 1.247 (air = 1). On escaping into the air it fumes strongly, owing to its forming with the aqueous vapor of the air a compound which is less volatile than water, and which consequently separates as

fog. Water at 0° C. absorbs 503 times its volume of hydrochloric acid gas, forming a fuming, powerfully acid solution which parts with a portion of its gas when the temperature is raised. Water absorbs hydrochloric acid gas with such rapidity that it rushes into a space containing this gas as into a vacuum. This may be shown by the following experiment: A wide tube of thin glass, closed at the top, is filled over mercury with *pure* hydrochloric acid gas, and, a small porcelain crucible being inserted under the tube, the tube with the crucible is lifted out of the mercury and lowered into a vessel of water. In this position it remains unaltered, as the tube is closed by the mercury in the crucible; but if the tube be raised out of the mercury so that its orifice is under water (as in *Preparation* 1) the water will rush in with such violence as to shatter the top of the tube. The success of this experiment depends upon the perfect purity of the hydrochloric acid gas; the least trace of air mixed with the gas forms an unabsorbed layer of indifferent gas above the rising column of liquid, thus not only checking the rapidity of absorption, but acting as a cushion to break the shock against the top of the tube.

Hydrochloric acid is employed in the laboratory chiefly in the form of its aqueous solution. The strong fuming acid possesses at 15° C. (59° F.) a specific gravity of 1.21, and contains about 43 per cent. of HCl. The commercial acid is frequently contaminated with sulphurous and sulphuric acids, free chlorine, arsenic, and iron.

If the saturated solution of hydrochloric acid be heated, it gives off gas and becomes weaker as the temperature rises, till at 110° C. (230° F.) under the normal pressure a solution containing 20.24 per cent. of HCl, and corresponding very closely with the formula $HCl,8OH_2$, distils over unchanged. If this acid, which distils at 110° C., be diluted with water and subjected to distillation, a weak acid comes over at first, and the acid in the retort becomes gradually stronger till it contains 20.24 per cent. of HCl, when it again distils unchanged at 110° C. It was long supposed that this solution with constant boiling-point represented a definite aquate or hydrate, but Roscoe and Ditmar have shown that this correspondence with the formula $HCl,8OH_2$ is a result of chance, and that, by varying the pressure, solutions of varying strength, but constant for each pressure, may be obtained. The lower the pressure the higher is the percentage of HCl contained in the residual acid.

The specific gravity of an aqueous solution of hydrochloric acid increases with the percentage of acid. In the following table the column headed d contains the specific gravities at 15° C. (59° F.), that headed p the corresponding percentages of hydrochloric acid. It is thus only necessary to determine the specific gravity of a sample of aqueous acid in order, by reference to the table, to ascertain its approximate strength:

Specific Gravity Table of Aqueous Hydrochloric Acid at 15° (Kolb).

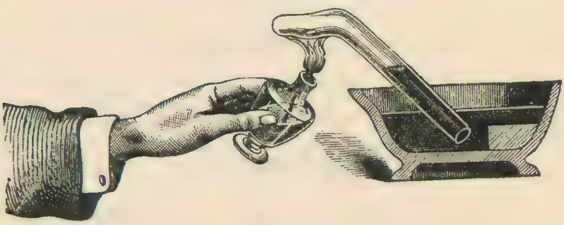
d.	*p.*	*d.*	*p.*
1.212	42.9	1.125	24.8
1.210	42.4	1.116	23.1
1.205	41.2	1.108	21.5
1.199	39.8	1.100	19.9
1.195	39.0	1.091	18.1
1.190	37.9	1.083	16.5
1.185	36.8	1.075	15.0
1.180	35.7	1.067	13.4
1.175	34.7	1.060	12.0
1.171	33.9	1.052	10.4
1.166	33.0	1.044	8.9
1.161	32.0	1.036	7.3
1.157	31.2	1.029	5.8
1.152	30.2	1.022	4.5
1.143	28.8	1.014	2.9
1.134	26.6	1.007	1.5

Hydrochloric acid gas is only partially decomposed by the passage of a series of electric sparks.

The composition of hydrochloric acid gas has been demonstrated by means of synthesis (1). It remains to show how it may be proved by analysis.

For this purpose, a measured volume of gaseous hydrochloric acid is introduced into a bent tube over mercury (Fig. 26). A piece of sodium is then pushed up through the mercury by means of a thin iron wire

FIG. 26.



till it lodges in the curved end of the tube. On heating that part of the tube by means of a flame, the sodium decomposes the gas, combining with the chlorine to form sodic chloride and liberating hydrogen. As soon as the reaction is complete, the tube is allowed to cool and the residual gas is measured, when it will be found that the original volume has been reduced by one-half. The residual gas may be inflamed or otherwise shown to possess the properties of hydrogen.

Suppose, therefore, in order to simplify the calculation, that the original volume of the gas, at standard temperature and pressure, was 2 litres:

2 litres of hydrochloric acid gas weigh . . .	36.5 criths.
Subtract the weight of 1 litre of residual hydrogen,	1.0 "
And there remain, ...	35.5 "

which is the weight of 1 litre of chlorine. One volume of chlorine therefore combines with one volume of hydrogen to form two volumes of hydrochloric acid gas.

Hydrochloric acid may be converted into salts termed chlorides by the action of certain metals as already described, and also by the action of the metallic hydrates or oxides:

$$\mathbf{O}KH + HCl = KCl + \mathbf{O}H_2.$$

Potassic hydrate.	Hydrochloric acid.	Potassic chloride.	Water.

$$\mathbf{Zn}O + 2HCl = \mathbf{Zn}Cl_2 + OH_2.$$

Zincic oxide.	Hydrochloric acid.	Zincic chloride.	Water.

Hydrochloric acid produces in the solutions of the salts of lead a white precipitate of plumbic chloride ($\mathbf{Pb}Cl_2$), soluble in excess of water. With mercurous salts it gives a white precipitate of mercurous chloride ($'\mathbf{Hg}'_2Cl_2$), insoluble in excess of water, but readily soluble if chlorine be passed into the solution. Ammonia causes this precipitate to blacken. With the soluble salts of silver, hydrochloric acid yields a white precipitate of argentic chloride (AgCl), insoluble in water, in chlorine water, and in nitric acid, but soluble in ammonia. This precipitate blackens when exposed to light.

CHAPTER XXIII.

DYAD ELEMENTS.

SECTION I.

OXYGEN, O_2.

Atomic weight = 16. *Molecular weight* = 32. *Molecular volume* $\square\square$. 1 *litre weighs* 16 *criths. Liquefies at* —136° C. (—212.8° F.) *under a pressure of* 22.5 *atmospheres. Atomicity* ''. *Evidence of atomicity*—

Water, ...	$\mathbf{O}H_2$.
Potassic hydrate, ...	$\mathbf{O}HK$.
Argentic oxide, ...	$\mathbf{O}Ag_2$.
Hypochlorous anhydride, ...	$\mathbf{O}Cl_2$

History.—Oxygen was discovered by Priestley in 1774, and a year later independently by Scheele. The name *oxygen*, "the acid-producer" (from ὀξύς, sour, and γεννάω, I bring forth) was given to it by Lavoisier, who regarded it as an essential constituent of all acids, a rule which subsequent discovery has shown to be subject to exception.

Occurrence.—Oxygen is the most plentiful and widely distributed of the elements. It is found in the free state, mechanically mixed with nitrogen, in the atmosphere, of which it constitutes slightly over a fifth part by volume. It occurs in combination in water, in most minerals, (forming nearly one-half by weight of the earth's crust), and in almost all animal and vegetable compounds.

Preparation.—1. When mercuric oxide ($\mathbf{Hg}O$) is heated to redness, it is decomposed into mercury and oxygen—

$$\underset{\text{Mercuric oxide.}}{2\mathbf{Hg}O} = 2Hg + O_2.$$

The operation may be performed in a retort of hard glass, and the oxygen collected over water at the pneumatic trough. This method, which was that first employed by Priestley, is too costly for ordinary use.

2. Many peroxides, when heated, lose a part of their oxygen, and are reduced to a lower stage of oxidation. This is the case with manganic peroxide ($\mathbf{Mn}O_2$), plumbic peroxide ($\mathbf{Pb}O_2$), and baric peroxide ($\mathbf{Ba}O_2$). The first of these peroxides is found in large quantities in nature, and may be advantageously employed as a source of oxygen. The decomposition cannot be effected in glass vessels, owing to the high temperature required. In order to obtain the oxygen, the manganic peroxide is placed in an iron bottle fitted with a delivery tube, and the bottle is heated to bright redness in a furnace. The manganic peroxide parts with one-third of its oxygen, undergoing reduction to trimanganic tetroxide—

$$\underset{\substack{\text{Manganic}\\\text{peroxide.}}}{3\mathbf{Mn}O_2} = \underset{\substack{\text{Trimanganic}\\\text{tetroxide.}}}{{}^{\text{iv}}(\mathbf{Mn}_3)^{\text{viii}}O_4} + O_2.$$

3. For laboratory purposes, oxygen is most conveniently prepared by heating potassic chlorate in a Florence flask or hard glass retort. The salt parts with the whole of its oxygen (39.18 per cent. of its weight), forming potassic chloride—

$$\underset{\substack{\text{Potassic}\\\text{chlorate.}}}{2\left\{\begin{matrix}\mathbf{O}Cl\\O\\\mathbf{O}K\end{matrix}\right.} = \underset{\substack{\text{Potassic}\\\text{chloride.}}}{2KCl} + 3O_2.$$

The gas may be collected as in *Preparation* 1. The salt fuses before giving off its oxygen. The heat required for the decomposition is somewhat high, particularly towards the close of the operation, and is apt to soften the glass retort. By mixing the chlorate, however, with about one-eighth of its weight of manganic peroxide, the oxygen is given off at a much lower temperature. In this case the chlorate does not fuse. The manganic peroxide is found unchanged at the end of the process, and its action probably consists in taking up oxygen to form a higher oxide, which immediately decomposes into manganic

peroxide and free oxygen. Other substances, such as ferric oxide and spongy platinum, also aid in liberating oxygen from potassic chlorate.

Commercial manganic peroxide is occasionally adulterated with coal-dust. When this adulterated peroxide is heated with potassic chlorate, sudden explosive combustion of the coal at the expense of the oxygen of the chlorate takes place, and from this cause fatal accidents have occurred. It is therefore advisable to test the manganic peroxide first by heating a small quantity with potassic chlorate in a test-tube.

4. When a non-salifiable peroxide of an electropositive element is heated with sulphuric acid, a sulphate of the lower and salifiable oxide is formed, and the excess of oxygen, above what is required for the salifiable oxide, is evolved. In this way manganic peroxide when heated with sulphuric acid parts with half its oxygen—

$$\underset{\text{Manganic peroxide.}}{2\mathbf{Mn}O_2} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2} = \underset{\text{Manganous sulphate.}}{2\mathbf{S}O_2Mno''} + \underset{\text{Water.}}{2\mathbf{O}H_2} + O_2.$$

An analogous reaction occurs when potassic dichromate is heated with sulphuric acid—

$$\underset{\text{Potassic dichromate.}}{2\left\{\begin{matrix}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{8\mathbf{S}O_2Ho_2} = \underset{\text{Potassic sulphate.}}{2\mathbf{S}O_2Ko_2} +$$

$$\underset{\text{Chromic sulphate.}}{2\mathbf{S}_3O_6('Cr'''_2O_6)^{vi}} + 3O_2 + \underset{\text{Water.}}{8\mathbf{O}H_2}.$$

It will assist the student to understand the mechanism of complicated reactions like the above, if he fixes his attention upon that portion of the equation which refers to the actual process under consideration—in this case the preparation of oxygen. Thus he would write the first of the above equations—

$$\underset{\text{Manganic peroxide.}}{\mathbf{Mn}O_2} = \underset{\text{Manganous oxide.}}{MnO} + \underset{\text{Oxygen.}}{O.}$$

and the second—

$$\underset{\text{Chromic anhydride.}}{2\mathbf{Cr}O_3} = \underset{\text{Chromic oxide.}}{\mathbf{Cr}_2O_3} + 3O.$$

The formation of manganous, potassic, and chromic sulphates, and of water, is necessary to the occurrence of the actual reactions; but the use of the above abbreviated forms of the equations will help the student to realize what is the essence of these processes—the reduction of a higher oxide to a lower and basic oxide with liberation of oxygen.

All the equations given in this chapter—with the exception of the above abbreviated forms—are what are known as *molecular* equations; that is to say, none but molecular quantities of the substances taking part in the reactions are therein represented, at least in the case of substances of known molecular weight. It is obvious that the proportions by weight would remain unaltered if the quantities employed in these equations were all halves. Thus in 1 we should have—

$$\mathbf{Hg}O = Hg + O,$$

the only objection being that O represents a semi-molecule of oxygen—a quantity which does not exist in the free state. Such equations are termed *atomic*. The use of atomic equations is often convenient and is quite unobjectionable if it be borne in mind that such equations are employed only as abbreviations.

5. When concentrated sulphuric acid is allowed to trickle slowly over fragments of brick contained in an earthenware retort heated to bright redness, the acid is decomposed into oxygen, sulphurous anhydride, and water (Deville and Debray)—

$$\underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Water.}}{OH_2} + O.$$

On passing the mixed gases through water, the sulphurous anhydride is absorbed, whilst the oxygen passes on and may be collected as usual. When this method is employed on the large scale, the concentrated solution of sulphurous anhydride thus obtained may be afterwards transferred to the leaden chambers and employed in the manufacture of sulphuric acid. (See *Sulphuric acid.*)

6. If a concentrated aqueous solution of bleaching powder be gently heated with a small quantity of cobaltic oxide (Co_2O_3), the whole of the oxygen contained in the bleaching powder will be given off—

$$\underset{\text{Bleaching powder.}}{Ca(OCl)Cl} = \underset{\text{Calcic chloride.}}{CaCl_2} + O.$$

The cobaltic oxide appears to undergo no change in the reaction, and the same quantity may be used repeatedly. The gas is evolved with great regularity. It is best, in order to avoid frothing, to employ a clear solution of bleaching powder. Cupric oxide may be substituted for cobaltic oxide.

7. It has been mentioned (2) that baric peroxide (BaO_2), when heated, parts with a portion of its oxygen—

$$\underset{\text{Baric peroxide.}}{BaO_2} = \underset{\text{Baryta.}}{BaO} + O.$$

By passing a current of air over the baryta thus obtained, whilst the temperature is allowed to fall below that required for the decomposition of baric peroxide, the baryta takes up oxygen and is reconverted into peroxide. Theoretically an unlimited quantity of oxygen may be obtained from the same quantity of baric peroxide by the alternate repetition of these processes (Boussingault). In practice, however, the baryta is found to combine with the silica of the porcelain tubes to form a silicate which is incapable of taking up oxygen.

8. A similar alternate method is that proposed by Tessié du Motay. When potassic manganate (MnO_2Ko_2) is heated in a current of steam, oxygen is evolved, whilst caustic potash and lower oxides of manganese remain. On heating the mixture of caustic potash and oxides of manganese with free access of air, oxygen is absorbed and the manganate is regenerated.

9. Oxygen may be obtained by the electrolysis of water acidulated with sulphuric acid (see Introduction, p. 106).

10. When a mixture of steam and chlorine is passed through a red-hot porcelain tube, the chlorine combines with the hydrogen of the water, liberating oxygen:

$$2OH_2 + 2Cl_2 = 4HCl + O_2.$$

The porcelain tube ought to be filled with fragments of porcelain in order to increase the heating surface. The gases issuing from the tube are washed by passing through a solution of caustic potash, by which the hydrochloric acid and the excess of chlorine are absorbed.

11. Oxygen is evolved in nature, in a remarkable manner, by the decomposition of atmospheric carbonic anhydride by the green leaves of plants under the influence of sunlight. The plant assimilates the carbon of the carbonic anhydride, whilst the oxygen escapes into the atmosphere. This decomposition may be shown experimentally by placing fresh mint or parsley under a glass cylinder inverted over a pneumatic trough, and filled with water saturated with carbonic anhydride. On exposing the whole to sunlight oxygen is liberated in minute bubbles from the leaves of the plant, and collects in the upper part of the cylinder.

Properties.—Oxygen is a colorless, tasteless, inodorous gas, slightly heavier than atmospheric air, its specific gravity being 1.10563 (air = 1). It is but slightly soluble in water; 1 volume of water at 0° C. dissolves about 0.04 volume of oxygen.

Oxygen possesses powerful chemical affinities, and has been made to combine with every known element except fluorine. Some few metals, like potassium and sodium, are attacked by dry oxygen at ordinary temperatures, and become covered with a coating of oxide; the majority remain bright under these circumstances. Many others become oxidized only when moisture is present to aid the oxygen. Others, like copper and mercury, combine with oxygen only at higher temperatures; whilst platinum, gold, and silver are not acted upon directly by oxygen at any temperature.

The chemical actions of atmospheric air are all dependent on the presence of oxygen, air being practically nothing more than oxygen diluted with about four times its bulk of nitrogen. These chemical actions are displayed in much greater intensity by undiluted oxygen. Combustion, for example, is chemical combination, sufficiently violent to be attended with evolution of heat and light. In the case of the combustion of a body in air, the presence of an indifferent diluent—nitrogen—greatly moderates the violence of the action; in the first place, by causing combination to take place more slowly, owing to the interposition of a number of molecules which do not participate in the reaction, and secondly, by lowering the temperature of the whole, the indifferent gas appropriating to itself part of the heat derived from chemical combination. In pure oxygen, all the phenomena of combustion are exhibited in their utmost intensity. Sulphur burns in air with a pale blue flame, emitting a feeble light; but in oxygen its flame be-

comes strongly luminous. The light emitted by phosphorus burning in oxygen is of such dazzling brilliancy that it can scarcely be supported by the eye. A match, extinguished but still glowing, bursts into flame when plunged into oxygen. Many substances incapable of undergoing combustion in air, burn readily in oxygen. If a bundle of thin iron wires, tipped with burning sulphur to start the combustion, be plunged into a jar of oxygen the iron will begin to burn, throwing off dazzling scintillations. The temperature developed in the combustion of iron is so high that if the jar of oxygen be closed below by a porcelain dish containing water, the globules of molten oxide will fall through the water and imbed themselves in the glaze of the porcelain.

Hydrogen burns in oxygen; and hence it is customary to term hydrogen a combustible gas and oxygen a supporter of combustion. But it may easily be shown that these terms are relative and interchangeable. If an inverted jar of hydrogen be lighted at the mouth and a jet of oxygen from a gas-holder be passed up through the burning hydrogen into the jar, the oxygen will ignite in the flame and will continue to burn inside the jar in the atmosphere of hydrogen. Flame is merely the visible manifestation of the chemical union of gases; this union can take place only at the surface of contact of the two gases, and its nature and manner will be the same, whether the hydrogen is streaming into the oxygen or the oxygen into the hydrogen.

The very high temperature produced in the chemical union of oxygen and hydrogen is turned to account in the oxy-hydrogen blowpipe. The hydrogen is burnt from a nozzle, through the centre of which a blast of oxygen passes. The flame thus produced possesses such a low illuminating power as to be scarcely visible in bright daylight; but its temperature is enormously high. Platinum readily fuses in the flame, and silver may be distilled by means of it—a method of purifying silver which was adopted by Stas in his classical researches on the atomic weights.

In all cases of combustion in oxygen, compounds known as oxides are formed. In the case of the combustion of hydrogen, the oxide is water, which is deposited as dew on the sides of the vessel in which the experiment is performed. If the gases are mixed before a light is applied, the combination takes place with explosion. This explosion is most violent when the two gases are employed in the proportions in which they combine to form water—two volumes of hydrogen to one of oxygen.

Oxygen is the only gas which can support respiration. An animal placed in air previously deprived of oxygen speedily dies. Pure oxygen at ordinary pressures may be inhaled with impunity, but compressed oxygen is a powerful poison.

Oxygen is rapidly absorbed by a solution of sodic dithionite (hydrosulphite) or by one of potassic pyrogallate, the liquid assuming in the latter case a deep brown color. By this means oxygen may be removed from mixtures of gases in which it is present. A solution of cuprous chloride in ammonia also absorbs oxygen, but more slowly, becoming of an intense blue color. If the colorless gas, nitric oxide, be added to free oxygen or to a mixture containing free oxygen, reddish fumes are

produced owing to the formation of higher oxides of nitrogen. These fumes are readily soluble in water.

ALLOTROPIC OXYGEN, *or* OZONE, O_3.

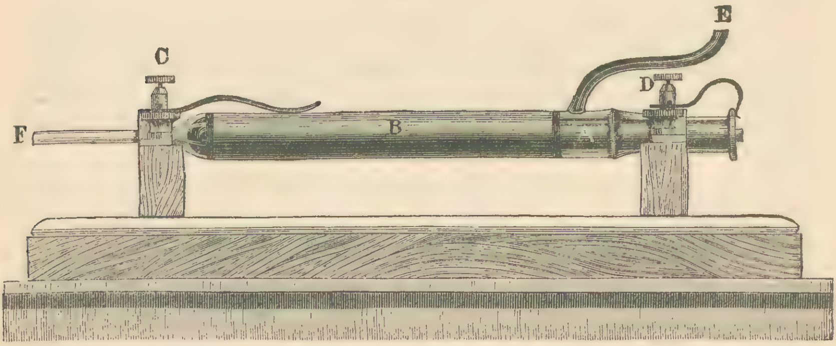
Molecular weight = 48. *Molecular volume* ◻◻. 1 *litre weighs* 24 *criths. Liquefies at* —105° C. (—157° F.) *under a pressure of* 125 *atmospheres.*

History.—In 1785 Van Marum first noticed that oxygen through which electric sparks had been passed acquired a peculiar odor. Schönbein in 1840 investigated the subject, and gave to the substance which is the cause of this odor the name *ozone* (ὄζειν, to smell). He showed that ozone is also contained in the oxygen evolved in the electrolysis of acidulated water, and that it is produced when phosphorus is allowed to oxidize slowly in moist air.

Occurrence.—Ozone is found in minute quantities in country air and in sea air. It is rarely present in the air of towns, as it is destroyed by the organic impurities which occur in such air.

Preparation.—1. Ozone is best obtained by the action of the silent electric discharge upon oxygen. A glass tube, *A* (Fig. 27), coated inside with tinfoil, or silvered internally, is surrounded by a second tube, *B*,

FIG. 27.



coated on the inside with tinfoil. This arrangement constitutes a species of Leyden jar, with double glass walls and a vacant space between them. The apparatus, which is known as a "Siemens induction tube," is so constructed that a gas, passed in at *E*, flows between the tubes and emerges at *F*. If, at the same time, the inner and outer coatings are connected, by means of the binding-screws *C* and *D*, with the terminals of an induction coil in action, the gas is subjected to a series of silent electrical discharges. When oxygen is thus treated, it is partially converted into ozone, which may be recognized by its peculiar odor and powerful oxidizing properties. If the ozonized oxygen be passed into a solution of potassic iodide, iodine is liberated with formation of potassic hydrate:

$$\underset{\text{Potassic iodide.}}{2KI} + \underset{\text{Water.}}{OH_2} + O = \underset{\text{Potassic hydrate.}}{2OKH} + I_2.$$

If a little starch has been added to the potassic iodide beforehand, the presence of the slightest trace of free iodine is instantly manifested by a deep blue coloration. This reaction is, however, common to most oxidizing agents.

It has hitherto proved impossible to convert the whole of the oxygen into ozone. Under the most favorable circumstances not more than one-fourth is thus converted.

The electric spark is not nearly so powerful an agent for the conversion of oxygen into ozone as the silent discharge. Indeed if the spark be allowed to pass through oxygen which has already been ozonized by the silent discharge, a considerable proportion of the ozone is reconverted into oxygen.

2. If one or two sticks of clean moist phosphorus be placed in a bottle of air or oxygen, a portion of the oxygen will, after the lapse of an hour or two, be converted into ozone. The phosphorus must then be removed and the gas washed with water to remove the phosphorous acid, otherwise the ozone will gradually disappear.

3. If water acidulated with sulphuric or chromic acid be electrolyzed, the oxygen evolved at the positive electrode is found to contain ozone. The quantity is, however, very small, not exceeding $\frac{1}{250}$ part of the weight of the oxygen.

4. Ozone is formed in very minute quantity during the evaporation of water (Gorup-Besanez), particularly when the water is dissipated in the form of spray. This probably accounts for the presence of ozone in sea-air, in which it may even bedetected by its odor.

The nature of the substance formed in these reactions remained for a long time unexplained. The first experiments which threw any real light on the subject were those of Andrews and Tait. The method employed by these investigators was as follows: The oxygen to be ozonized was inclosed in a tube terminating in a capillary siphon containing sulphuric acid. By means of the rise and fall of this liquid in the limbs of the siphon, the changes of volume of the gas inclosed in the tube could be measured. Two platinum wires were fused into the oxygen tube, and by means of these a silent electric discharge was passed through the oxygen. It was observed that, when the oxygen was ozonized, contraction occurred, never, however, exceeding $\frac{1}{12}$ of the entire volume. On heating the ozonized oxygen to 300° C. (572° F.), it regained its original volume, and no longer contained ozone. A thin sealed glass tube containing a solution of potassic iodide was then introduced into the oxygen tube, and after the maximum ozonization had been attained, the sealed tube was broken. The ozone liberated iodine from the solution, but no change of volume was observed in the gas, and on heating to 300° C. (572° F.) no expansion took place. The amount of iodine liberated was exactly equivalent to the oxygen which had apparently disappeared in the contraction which took place when ozone was formed. It was thus evident that ozone in acting on potassic

iodide yielded its own volume of ordinary free oxygen *plus* a certain volume of oxygen employed in the oxidation, this last volume being equal to the original contraction. In order to determine the molecular weight of ozone, it was therefore only necessary to know the relation of these two volumes to each other, but for this purpose the volume of ozone present in the gas had to be ascertained. This was first accomplished by Soret, who found that oil of turpentine has the property of absorbing the entire molecule of ozone, whilst it has no action on the unchanged oxygen present in the mixture. A sample of ozonized oxygen was divided into two parts: one of these was subjected to the action of heat, and the other to the absorbent effect of oil of turpentine. It was found that the contraction which took place with the oil of turpentine was exactly twice as great as the expansion caused by heat. From this it follows that three volumes of oxygen condense to form two of ozone, or, the molecule of ozone contains three atoms (O_3). The oxidizing effect of ozone on potassic iodide is therefore to be expressed as follows:

$$\underset{\text{Ozone.}}{O_3} + \underset{\substack{\text{Potassic}\\\text{iodide.}}}{2KI} + \underset{\text{Water.}}{OH_2} = \underset{\text{Oxygen.}}{O_2} + I_2 + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{2OKH.}$$

Properties.—Ozone is a colorless gas possessing an odor somewhat resembling that of chlorine. It has never been obtained in the pure state (unless the liquid ozone described further on represents the pure substance), but is always diluted with a large excess of oxygen. When dry it may be preserved for a long time. At a temperature of about 250° C. (482° F.) it is at once reconverted into ordinary oxygen. It is also decomposed by contact with the peroxides of manganese and lead at ordinary temperatures, these peroxides apparently undergoing no change in the process. Hydroxyl and ozone mutually decompose each other with evolution of oxygen:

$$\underset{\text{Ozone.}}{O_3} + \underset{\text{Hydroxyl.}}{\begin{cases} OH \\ OH \end{cases}} = \underset{\text{Water.}}{OH_2} + \underset{\text{Oxygen.}}{2O_2.}$$

Ozone is a powerful oxidizing agent. Organic matters are rapidly corroded by it. Most metals are oxidized by its action. Silver becomes covered with a film of argentic peroxide, which in its turn has the property of decomposing ozone like the peroxides above mentioned. Mercury is also acted upon by ozone, the smallest trace of which causes the mercury to lose its brilliant surface and to adhere to glass. The oxidizing action of ozone depends on the readiness with which it is decomposed into oxygen:

$$O_3 = O_2 + O.$$

The molecule of oxygen thus formed is stable and inert; whilst the atom, being in the nascent state, with its bonds at liberty, is ready to combine with any suitable atoms that may be present. No contraction

takes place in these oxidations, O_3 and O_2 alike representing two volumes.

Paper moistened with manganous sulphate turns brown when exposed to the action of ozone, owing to the formation of hydrated manganic peroxide. Paper stained black with plumbic sulphide becomes white when acted upon with ozone, the plumbic sulphide (**Pb**S) being oxidized to the sulphate (**S**O_2Pbo″).

When subjected to a temperature of —105°, produced by the evaporation of liquid ethylene, and a pressure of 125 atmospheres, ozone condenses to an indigo-blue liquid, which only slowly evaporates at ordinary pressure (Hautefeuille and Chappuis).

Some chemists have described a third variety of oxygen, to which they gave the name *antozone;* but antozone has been conclusively shown to be nothing more than hydroxyl.

COMPOUNDS OF OXYGEN WITH HYDROGEN.

WATER, *Hydric Oxide.*

H—O—H **O**H_2.

Molecular weight =18. *Molecular volume* $\square\square$. 1 *litre of water-vapor weighs* 9 *criths. Fuses at* 0° C. *Boils at* 100° C.

History.—Water was one of the four elements of the ancients. Priestley first observed that when hydrogen is burned in a vessel containing air or oxygen, drops of water are deposited on the sides of the vessel. The compound nature of water was first conclusively demonstrated by Cavendish, Watt, and Lavoisier.

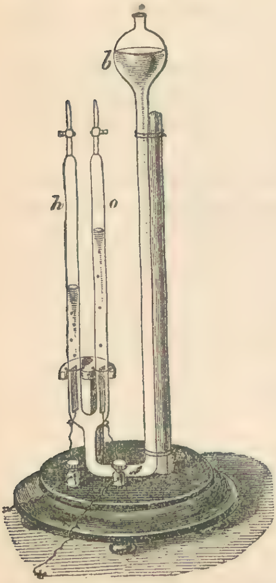
Occurrence.—Water in all its forms is widely diffused in nature. In the solid form it exists as snow or ice; in the liquid state it constitutes seas, lakes and rivers; whilst as a colorless gas it is contained in all naturally occurring air, however dry. In a state of minute subdivision it exists as clouds and mist. In combination it is found in various minerals, particularly in those of the class known as *zeolites*, as water of crystallization.*

Formation.—1. Water is formed by the direct union of hydrogen and oxygen (see *Oxygen*, p. 165). This union takes place in the proportion of 2 volumes of hydrogen to 1 of oxygen. Before, however, proving this fact directly by synthesis, it will be convenient to prove it indirectly by analysis, employing the method of electrolysis. For this purpose the apparatus represented in Fig. 28, which consists of a U-tube *ho* containing electrodes of platinum and connected with a reservoir globe *b*, may be employed. Water acidulated with sulphuric acid is poured into the globe and allowed to fill the two limbs of the U-tube,

* It is equally possible, however, that these minerals merely contain the *elements of water*, which are evolved as water when the mineral is heated; in other words, the water, as such, is not pre-existent in the mineral.

after which the glass stopcocks are closed. On passing the electric current, the gases will be evolved from the electrodes and will collect in the limbs of the U-tube, the displaced water rising into the globe. The hydrogen, which is evolved at the negative electrode, will be found to occupy a volume twice as great as that of the oxygen, which is evolved at the positive electrode. The quantity of oxygen is, however, slightly below the theoretical amount, owing to the greater solubility of oxygen in water, and also owing to the fact that a small portion of this gas is liberated as ozone, which occupies only two-thirds of the volume of ordinary oxygen. On opening the stopcocks the pressure of the water forces out the gases, which may be identified by the usual tests.

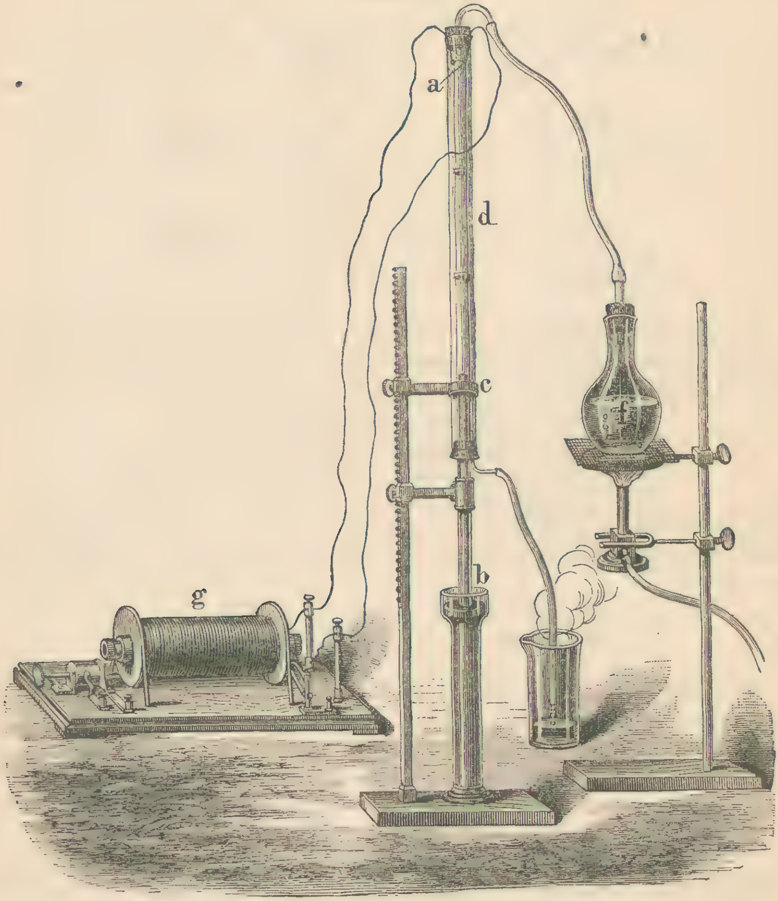
FIG. 28.



After arriving at these results, the fact that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam, may be shown by means of the apparatus represented in Fig. 29. A tube ab, closed at one end and known as a *eudiometer*, is filled with mercury and inverted over a tall vessel of mercury. At the upper end of the eudiometer, platinum wires are fused through the glass for the purpose of passing an electric spark. A portion of the tube, ac, having a length of about 45 centimetres measured from the top, is divided by marks on the glass into three parts of equal capacity. The whole of this portion of the eudiometer is surrounded by a wider glass tube d, through which steam from the flask f can be passed. The eudiometer with the steam-jacket is supported by the lower clamp, so that, by shifting this clamp, the whole can be raised or lowered in the vessel of mercury. The upper clamp is not shifted during the experiment; it fits loosely round the tube, and serves only to mark a fixed height above the surface of the mercury in the vessel. When the experiment is to be performed, the apparatus is adjusted so that the position of this clamp coincides with the lowest of the three divisions on the eudiometer, and steam is passed into the steam-jacket. The mixture of gases obtained by the electrolysis of water is now introduced so as to fill the three divisions of the eudiometer. The gases are thus measured at 100° C., and the height of the column of mercury cb in the eudiometer tube is marked by the upper clamp. The eudiometer is now lowered until the open end presses against a pad of india rubber at the bottom of the mercury vessel, the object of this being to prevent the expulsion of the mercury from the tube during the explosion. On passing the spark, the gases combine and a flash of light is seen to fill the tube, but no sound is heard. The tube is now raised till the top of the column of mercury again coincides with the upper clamp, when it will be found that the

aqueous vapor fills two divisions of the tube. This measurement is in every respect comparable with the first, since the mixed gases on the one hand and the aqueous vapor formed by their union on the other, are both measured at the same temperature, 100° C., and under the

FIG. 29.



same pressure—that of the atmosphere less that of the column of mercury *cb*. The aqueous vapor has no tendency to condense to water, since it is measured under reduced pressure.

It is thus found that 3 volumes of the electrolytic mixture of oxygen and hydrogen, consisting of 1 volume of the former to 2 of the latter, combine to yield 2 volumes of vapor of water.

On cutting off the supply of heating steam, the aqueous vapor will condense and the mercury will rise and fill the eudiometer,* the volume occupied by the condensed water being inappreciable.

* Always supposing, of course, that the height of the eudiometer above the surface of the mercury is not greater than that of the barometer less the tension of aqueous vapor for the prevailing temperature.

2. Water is not only formed during the combustion of hydrogen in oxygen or air, but also when any compound containing hydrogen is burned in oxygen or air. If the elements combined with the hydrogen are readily oxidizable, they will also unite with the oxygen. The following reactions illustrate this:

CH_4	+	$2O_2$	=	CO_2	+	$2OH_2$.
Marsh-gas.				Carbonic anhydride.		Water.

SiH_4	+	$2O_2$	=	SiO_2	+	$2OH_2$.
Siliciuretted hydrogen.				Silicic anhydride.		Water.

$2SH_2$	+	$3O_2$	=	$2SO_2$	+	$2OH_2$.
Sulphuretted hydrogen.				Sulphurous anhydride.		Water.

3. Water is formed as a secondary product in numberless other chemical reactions, as for instance in the action of acids on the hydrates of the metals:

OKH	+	HCl	=	OH_2	+	KCl.
Potassic hydrate.		Hydrochloric acid.		Water.		Potassic chloride.

In like manner it is produced when the elements of water are eliminated from some compounds under the influence of heat or dehydrating agents:

$CaHo_2$	=	CaO	+	OH_2.
Calcic hydrate.		Calcic oxide.		Water.

4. Water is formed when certain oxides are heated in a current of hydrogen. The oxygen combines with the hydrogen to form water, and the metal is reduced to the metallic state. Thus:

CuO	+	H_2	=	Cu	+	OH_2
Cupric oxide.						Water.

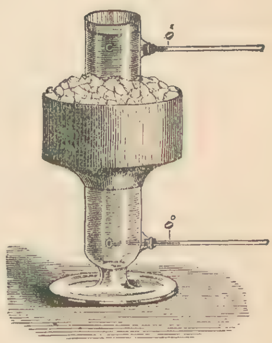
This reaction has been employed to determine the proportions by weight in which oxygen and hydrogen combine to form water. For this purpose a weighed quantity of cupric oxide is heated to redness in a current of perfectly dry hydrogen. The water which is formed in the reaction is absorbed in a weighed tube filled with some substance which has a powerful affinity for water, such as phosphoric anhydride or pumice moistened with sulphuric acid. The increase in weight of this tube gives the weight of water formed. The loss of weight of the tube with the cupric oxide determines the weight of oxygen consumed. The difference of these two values is the weight of hydrogen. In this way it has been found that 1 part by weight of hydrogen combines with 8 parts by weight of oxygen to form water.

Properties.—Pure water is a tasteless, inodorous liquid. In layers

of only moderate thickness it appears colorless; but when viewed in a layer several yards thick, it is seen to possess a peculiar bluish-green tint, somewhat resembling that of the edge of a sheet of window-glass. Water solidifies at 0° C. to ice, and boils at 100° C. under a pressure of 760 millimetres. The melting of ice and the boiling of water are employed to fix the points of 0° and 100° on the centigrade thermometer. Water is a bad conductor of heat and electricity. The rapid equalization of temperature which takes place in a mass of water, particularly when heat is applied to it from beneath, is due to convection currents.

Between the temperatures of 0° and 4° C. (32°–39° F.) water forms a remarkable exception to the law of expansion of bodies under the influence of heat, inasmuch as between these temperatures it contracts when heated, and expands in cooling. Above the temperature of 4° C. (39°F.) it expands in the usual manner when heated. This point of 4° C. (39° F.) is therefore known as the point of maximum density of water, and it is to this density (= 1) that the densities of solids and liquids are referred. The fact that the density of water is greatest at 4° C. (39° F.) may be shown by the following experiment. A tall glass cylinder (Fig. 30) filled with water of ordinary temperature, is furnished with two thermometers, one at the surface, the other at the bottom, of the liquid. Round the middle of the vessel on the outside is a second vessel fills with a freezing mixture. When the cold is applied, it will be seen that the lower thermometer begins to sink, whilst the upper one remains almost stationary, and this continues till the lower thermometer registers 4° C., when the temperature at the bottom of the vessel remains constant. After a short time, the upper thermometer begins to fall and does not stop till the freezing point is reached and ice is formed.

FIG. 30.



In solidifying, water undergoes sudden expansion. The specific gravity of water at 0° C. is 0.99987; that of ice at the same temperature is 0.91662. Most other substances contract in passing from the liquid to the solid state. Ice floats readily on the surface of water. The force which can be exerted by the expansion of water in freezing is enormous. A cast-iron shell filled with water and closed by means of a screw may be burst by exposing it to a freezing temperature. The splitting and crumbling of rocks in winter is, in like manner, produced by the freezing and expansion of the water which has penetrated into their crevices.

The solidification of water is, in reality, a crystallization, though it is difficult to obtain ice in distinct crystalline forms. These may be seen, however, in the case of snow, the flakes of which when magnified exhibit the form of six-pointed stars. The crystallographical system is hexagonal.

Water is an excellent solvent for a great number of substances, and

in this character plays a most important part both in nature and in the laboratory. The water which filters through rocks and soils extracts from these a portion of their soluble constituents. The dissolved substances are carried by rivers into the sea or into inland lakes without outlet. In every case evaporation goes on, producing concentration, and the water is returned in a distilled form as rain or dew to the land to repeat this process of extraction. In this way the sea and the salt lakes have received the solid substances held in solution, the quantity of which is constantly, though very slowly increasing. (For a description of the various substances contained in natural waters, see *Calcium.*)

The subject of solubility of salts in water has been treated of at some length in the Introduction (p. 126).

Reactions.—1. By the action of water many metallic oxides are converted into hydrates:

$$\underset{\text{Potassic oxide.}}{\mathbf{O}K_2} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Potassic hydrate.}}{2\mathbf{O}KH.}$$

$$\underset{\text{Baric oxide.}}{\mathbf{Ba}O} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Baric hydrate.}}{\mathbf{Ba}Ho_2.}$$

2. It transforms many anhydrides into acids:

$$\underset{\text{Nitric anhydride.}}{\mathbf{N}_2O_5} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Nitric acid.}}{2\mathbf{N}O_2Ho.}$$

$$\underset{\text{Sulphuric anhydride.}}{\mathbf{S}O_3} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2.}$$

$$\underset{\text{Phosphoric anhydride.}}{\mathbf{P}_2O_5} + \underset{\text{Water.}}{3\mathbf{O}H_2} = \underset{\text{Phosphoric acid.}}{2\mathbf{P}OHo_3.}$$

3. It also unites molecularly, as water of crystallization, with many compounds to form aquates (see p. 45), as in the following instances:

$\mathbf{Ba}Cl_2 2\mathbf{O}H_2$, ... Baric chloride.
$\mathbf{S}O_2Nao_2,10\mathbf{O}H_2$, ... Sodic sulphate.
$\mathbf{S}_4O_8Ko_2('Al'''_2O_6)^{vi},24\mathbf{O}H_2$, . . Alum.

For a description of some other subjects connected with water—latent heat of water, and of steam, tension of aqueous vapor, absorption of gases by water, etc., see Introduction.

HYDROXYL, *Hydric Peroxide.*

$$\text{H—O}\vdots\text{O—H} \qquad \text{Ho}_2 \text{ or} \begin{cases} \text{OH} \\ \text{OH.} \end{cases}$$

Probable molecular weight = 34.

History.—Hydroxyl was discovered by Thenard in 1818.

Occurrence.—It occurs in very small quantities in the atmosphere, and in dew, rain, and snow.

Preparation.—1. A dilute solution of hydroxyl may be obtained by passing a current of carbonic anhydride through water in which baric peroxide is suspended:

$$\underset{\text{Baric peroxide.}}{\begin{cases} \text{O} \\ \text{O} \end{cases}\!\text{Ba}''} + \underset{\text{Carbonic anhydride.}}{\text{CO}_2} + \underset{\text{Water.}}{\text{OH}_2} = \underset{\text{Baric carbonate.}}{\text{COBao}''} + \underset{\text{Hydroxyl.}}{\begin{cases} \text{OH} \\ \text{OH.} \end{cases}}$$

2. The most convenient method of preparing hydroxyl consists in dissolving *moist* hydrated baric peroxide in dilute sulphuric acid (Thomsen, *Ber. d. deutsch. chem. Ges.*, 7, 73). The pure moist hydrated baric peroxide, which should be preserved moist from the time of its preparation, is gradually added to the dilute sulphuric acid (1 part of concentrated acid to 5 of water), care being taken to leave the acid slightly in excess. The liquid is filtered from the baric sulphate, and the excess of sulphuric acid is removed from the filtrate by precipitating exactly with baryta-water. The liquid, again filtered from the baric sulphate, now contains nothing but hydroxyl and water. The water must be removed by evaporation at ordinary temperatures *in vacuo* over sulphuric acid, as hydroxyl is rapidly decomposed by boiling. In this way the solution may be concentrated till a specific gravity of 1.452 is attained, when the liquid evaporates without change in the composition of the residue.

Properties.—Hydroxyl is a colorless, slightly syrupy liquid, devoid of odor, and possessing a strong metallic taste. It bleaches and blisters the skin. It does not solidify at —30° C. (—22° F.). At ordinary temperatures it is gradually and spontaneously decomposed into oxygen and water; when heated to 100° C. this decomposition takes place with explosive violence. When diluted with water, or in presence of a small quantity of sulphuric acid, it is much more stable.

Like ozone, and all other bodies which are formed with absorption of heat, hydroxyl is particularly sensitive to catalytic action. Platinum, or carbon, in a finely divided state, effects its instantaneous decomposition into oxygen and water, these substances apparently undergoing no change in the process. Platinum does not possess any marked affinity for the elements of hydroxyl, nor does carbon at ordinary temperatures. On the other hand, iron, tin, and antimony are without action on hydroxyl, though their affinity for oxygen is very great.

The general characteristics of hydroxyl are those of a powerful oxi-

dizing agent. Finely divided metallic arsenic is converted by it into arsenic acid, with evolution of heat and light. Black plumbic sulphide (PbS) is converted into the white sulphate (SO_2Pbo''). For this reason hydroxyl is employed in restoring old paintings in which the white lead has, in course of time, been blackened by sulphurous exhalations. It also bleaches organic coloring matters, changing the color of dark hair to pale gold, a property which has led to its use as a hair dye.

But it also acts as a deoxidizing agent. Argentic oxide and hydroxyl mutually decompose each other, yielding metallic silver, water, and free oxygen.

$$\underset{\text{Argentic oxide.}}{OAg_2} + \underset{\text{Hydroxyl.}}{\left\{\begin{matrix} OH \\ OH \end{matrix}\right.} = 2Ag + \underset{\text{Water.}}{OH_2} + O_2.$$

Silver has a very slight affinity for oxygen, and its oxide is easily decomposed. The atom of oxygen given off by the hydroxyl combines with that of the oxide of silver to form a molecule of free oxygen, liberating metallic silver. By this reaction Brodie first demonstrated the diatomic character of the oxygen molecule; for if an excess of either reagent be employed, this excess remains unaltered. The oxides of gold and platinum behave similarly with hydroxyl. These reactions take place with almost explosive violence.

An analogous mutual decomposition occurs when hydroxyl is brought in contact with various peroxides, such as those of manganese and lead. The hydric peroxide is reduced to water, and the metallic peroxide to the salifiable oxide, whilst the two oxygen atoms thus liberated unite to form a molecule of oxygen as in the cases already described:

$$\underset{\text{Hydroxyl.}}{\left\{\begin{matrix} OH \\ OH \end{matrix}\right.} + \underset{\text{Manganic peroxide.}}{MnO_2} = \underset{\text{Water.}}{OH_2} + \underset{\text{Manganous oxide.}}{MnO} + O_2.$$

A similar case is the mutual decomposition of ozone and hydroxyl with formation of water and liberation of oxygen (see p. 168).

Hydroxyl precipitates the hydrates of calcium, barium, and strontium from their solutions in the form of peroxides:

$$\underset{\text{Baric hydrate.}}{BaHo_2} + \underset{\text{Hydroxyl.}}{\left\{\begin{matrix} OH \\ OH \end{matrix}\right.} = \underset{\text{Baric peroxide.}}{\left\{\begin{matrix} O \\ O \end{matrix}\right. Ba''} + \underset{\text{Water.}}{2OH_2}.$$

If to a solution of hydroxyl acidulated with sulphuric acid a few drops of potassic dichromate be added, the unstable compound, perchromic acid, is formed. On agitating the mixture with ether, the perchromic acid will be extracted from the aqueous solution, imparting to the supernatant ether a magnificent but fugitive blue color. This reaction is characteristic of hydroxyl, as no other known substance effects the oxidation of chromic to perchromic acid.

Hydroxyl, like other oxidizing agents, liberates iodine from potassic iodide, as may be shown by the blue color which is produced when

starch-paste has been added to the solution of the iodide. Hydroxyl is, however, the only oxidizing agent which can liberate iodine in presence of ferrous sulphate.

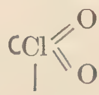
Hydroxyl is soluble in ether, and may be extracted from an aqueous solution by shaking with this solvent. The ethereal solution is more stable than the aqueous solution, and may be distilled without decomposition.

COMPOUNDS OF CHLORINE WITH OXYGEN AND HYDROXYL.

Chlorine forms several compounds both with oxygen alone and with oxygen and hydroxyl; but none of these can be produced by direct combination. The following list contains all that are known:

Hypochlorous anhydride, . . $\mathbf{O}Cl_2$. Cl—O—Cl.

Chloric peroxide, ... $'\mathbf{O}'(OCl)$ Cl—O—O—

or $'''\mathbf{Cl}^{iv}O_2$  *

Hypochlorous acid, . $\mathbf{O}ClH$, or $\mathbf{Cl}Ho$. H—O—Cl

Chlorous acid,† . . $\mathbf{O}ClHo$ or $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}H.\end{matrix}\right.$ H—O—O—Cl

Chloric acid, . . $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ho\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{O}Cl\\ O\\ \mathbf{O}H\end{matrix}\right.$. H—O—O—O—Cl

Perchloric acid, . . $\left\{\begin{matrix}\mathbf{O}Cl\\ O\\ \mathbf{O}Ho\end{matrix}\right.$ or $\left\{\begin{matrix}\mathbf{O}Cl\\ O\\ O\\ \mathbf{O}H\end{matrix}\right.$. H—O—O—O—O—Cl.

HYPOCHLOROUS ANHYDRIDE.

$\mathbf{O}Cl_2$.

Molecular weight = 87. *Molecular volume* ☐☐. 1 *litre of hypochlorous anhydride vapor weighs* 43.5 *criths. Boils about* 20° C. (68° F.).

Preparation.—Hypochlorous anhydride is obtained by passing chlorine over mercuric oxide at a low temperature:

* See *Periodates. Atomicity of Iodine.*

† *Chlorous anhydride*, Cl_2O_3, has not been prepared. What was formerly believed to be this compound has been conclusively shown to be nothing more than a mixture of chloric peroxide with free chlorine (Garzarolli-Thurnlackh, *Liebig's Annalen*, **209**, 184).

$$\underset{\text{Mercuric oxide.}}{2\mathbf{Hg}O} + 2Cl_2 = \underset{\text{Mercuric oxychloride.}}{\left\{\begin{matrix}\mathbf{Hg}Cl \\ O \\ \mathbf{Hg}Cl\end{matrix}\right.} + \underset{\text{Hypochlorous anhydride.}}{\mathbf{O}Cl_2}.$$

The mercuric oxide, which must be prepared by precipitation and dried at a temperature not exceeding 300° C. (572° F.), is conveniently contained in a horizontal tube through which a current of chlorine thoroughly dried by sulphuric acid slowly passes. The apparatus terminates in a U-tube surrounded by a freezing mixture, and in this tube the hypochlorous anhydride, liquefied by cold, collects.

Properties.—Hypochlorous anhydride is, at ordinary temperatures, a yellowish gas, possessing an odor somewhat resembling that of chlorine. By means of a freezing mixture it may be condensed to an orange-red liquid boiling about 20° C. (68° F.). It is a very unstable compound, and decomposes readily into its elements with explosion and evolution of heat. A slight shock, even the scratch of a file on the vessel in which it is contained, is often sufficient to determine its violent explosion. Exposure to direct sunlight has the same effect. The application of a flame also produces explosion, but with less violence. Arsenic, phosphorus, and the alkali metals ignite in contact with it, at the same time causing its explosion.

Water dissolves 200 times its volume of the gas, forming a yellow solution of hypochlorous acid, which possesses powerful bleaching and oxidizing properties.

CHLORIC PEROXIDE.

$$'\mathbf{O}'(OCl) \text{ or } '''\mathbf{Cl}^{iv}O_2.$$

Molecular weight = 67.5. *Molecular volume* $\square\!\square$. 1 *litre of chloric peroxide vapor weighs* 33.75 *criths. Boils at* 20° C. (68° F.).

History.—This compound was discovered by Davy in 1815.

Preparation.—Chloric peroxide is obtained by the action of concentrated sulphuric acid on potassic chlorate:

$$\underset{\text{Potassic chlorate.}}{3\left\{\begin{matrix}\mathbf{O}Cl \\ \mathbf{O}Ko\end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2} = \underset{\text{Potassic perchlorate.}}{\left\{\begin{matrix}\mathbf{O}Cl \\ O \\ \mathbf{O}Ko\end{matrix}\right.} + \underset{\text{Hydric potassic sulphate.}}{2\mathbf{S}O_2HoKo} + \underset{\text{Water.}}{\mathbf{O}H_2} + \underset{\text{Chloric peroxide.}}{2'\mathbf{O}'(OCl)}.$$

The finely powdered potassic chlorate (1 part) is added in small portions to the concentrated sulphuric acid (5 parts), avoiding any rise of temperature. On very gently warming the retort containing the mixture, by surrounding it with warm water, the gas is evolved. Care must be taken that the level of the liquid inside the retort is higher than that of the water outside, otherwise an explosion may occur owing to the heating of the gas.

Properties.—Chloric peroxide is a greenish-yellow gas, possessing an irritating odor. It must be collected by displacement, as it attacks mercury and is soluble in water, which takes up twenty times its volume of the gas. Exposed to the cold of a mixture of snow and salt, it condenses to a dark-red liquid which solidifies in a bath of liquid carbonic anhydride and ether.

It is a very unstable and dangerous compound, frequently exploding from the slightest cause. It is a powerful oxidizing agent. Phosphorus, organic and other combustible substances, ignite when brought in contact with it. If a drop of concentrated sulphuric acid be allowed to fall on a mixture of equal parts of potassic chlorate and sugar (separately powdered and cautiously mixed on a card with a feather), the chloric peroxide thus liberated ignites the sugar, and the whole mass deflagrates brilliantly.

If the aqueous solution of chloric peroxide be saturated with a base, a mixture of chlorate and chlorite is formed:

$$\underset{\text{Potassic hydrate.}}{2\mathbf{O}KH} + \underset{\text{Chloric peroxide.}}{2'\mathbf{O}'(OCl)} = \underset{\text{Potassic chlorate.}}{\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Ko\end{matrix}\right.} + \underset{\text{Potassic chlorite.}}{\mathbf{O}ClKo} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

As the molecular formula of chloric peroxide, deduced from its vapor-density, is ClO_2, this compound can be formulated only on the supposition that its gaseous molecule contains either one or three unsatisfied bonds.*

HYPOCHLOROUS ACID.

$\mathbf{O}ClH$ or $ClHo$.

Molecular weight = 52.5.

Preparation.—1. Hypochlorous acid is formed by the action of water on hypochlorous anhydride:

$$\underset{\text{Hypochlorous anhydride.}}{\mathbf{O}Cl_2} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Hypochlorous acid.}}{2ClHo.}$$

* Several similar cases are known, thus:

Nitric oxide, ...	$'\mathbf{N}''O$ or $'''\mathbf{N}''O$.
Nitric peroxide (at 140°), ...	$'\mathbf{N}^{iv}O_2$ or $'''\mathbf{N}\left.\begin{matrix}O\\O\end{matrix}\right\}$
Hypovanadic chloride, ...	$'\mathbf{V}^{iv}Cl_4$.
Molybdic pentachloride, ...	$'\mathbf{Mo}^{v}Cl_5$.
Tungstic pentachloride, ...	$'\mathbf{W}^{v}Cl_5$.

The above are the molecular formulæ of these compounds as deduced from their vapor-densities, and in every case the presence of an odd number of unsatisfied bonds must be assumed. It is perfectly conceivable, however, that in the liquid or solid state, two such molecules mutually satisfy each other's affinity, so as to produce a saturated molecule of twice the molecular weight. In fact, in the case of nitric peroxide, the vapor-density just above the boiling point of this compound corresponds rather with the formula $\left\{\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right.$ than with the formula $'\mathbf{N}^{iv}O_2$. Nitric oxide, and chloric peroxide, in some of their reactions, behave as if they possessed molecular formulæ twice as great as those deduced from their vapor-densities.

2. If chlorine water be shaken with an excess of precipitated mercuric oxide, the yellow color of the solution rapidly disappears, and hypochlorous acid along with mercuric oxychloride is formed:

$$\underset{\text{Mercuric oxide.}}{2\mathbf{Hg}O} + \underset{\text{Water.}}{\mathbf{O}H_2} + 2Cl_2 = \underset{\text{Mercuric oxychloride.}}{\begin{cases}\mathbf{Hg}Cl \\ O \\ \mathbf{Hg}Cl\end{cases}} + \underset{\text{Hypochlorous acid.}}{2ClHo.}$$

The solution of hypochlorous acid may be decanted from the insoluble oxychloride. If only 1 molecule of mercuric oxide is employed for every 2 molecules of chlorine, hypochlorous acid is formed as before; but a chloride instead of an oxychloride of mercury is formed, and remains in solution along with the hypochlorous acid. Thus:

$$\underset{\text{Mercuric oxide.}}{\mathbf{Hg}O} + \underset{\text{Water.}}{\mathbf{O}H_2} + 2Cl_2 = \underset{\text{Mercuric chloride.}}{\mathbf{Hg}Cl_2} + \underset{\text{Hypochlorous acid.}}{2ClHo.}$$

3. Another method consists in adding to a solution of bleaching-powder ($\mathbf{Ca}(OCl)Cl$) dilute nitric acid in quantity sufficient to saturate half the calcium:

$$\underset{\text{Bleaching-powder.}}{2\mathbf{Ca}(OCl)Cl} + \underset{\text{Nitric acid.}}{2\mathbf{N}O_2Ho} = \underset{\text{Calcic chloride.}}{\mathbf{Ca}Cl_2} + \underset{\text{Calcic nitrate.}}{\begin{cases}\mathbf{N}O_2 \\ Cao'' \\ \mathbf{N}O_2\end{cases}} + \underset{\text{Hypochlorous acid.}}{2ClHo.}$$

On subjecting the mixture to distillation, an aqueous solution of hypochlorous acid passes over.

Properties.—Hypochlorous acid has not been prepared in a state of purity. The aqueous solution produced by the absorption of hypochlorous anhydride in water is a yellow liquid of a penetrating odor, possessing powerful oxidizing properties. Black plumbic sulphide is changed by it into white plumbic sulphate. Only the dilute aqueous solution can be distilled without decomposition.

Hypochlorous and hydrochloric acids mutually decompose each other, yielding chlorine and water:

$$\underset{\text{Hypochlorous acid.}}{ClHo} + \underset{\text{Hydrochloric acid.}}{HCl} = Cl_2 + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

The chlorine is thus evolved from both compounds.

In like manner a mutual decomposition takes place between hypochlorous acid and argentic oxide, both compounds giving off oxygen:

$$\underset{\text{Argentic oxide.}}{\mathbf{O}Ag_2} + \underset{\text{Hypochlorous acid.}}{2ClHo} = \underset{\text{Argentic chloride.}}{2AgCl} + \underset{\text{Water.}}{\mathbf{O}H_2} + O_2.$$

Hypochlorites.—Hypochlorous acid converts metallic oxides and hydrates into hypochlorites:

$\mathbf{O}KH$	+	$ClHo$	=	$ClKo$	+	$\mathbf{O}H_2$.
Potassic hydrate.		Hypochlorous acid.		Potassic hypochlorite.		Water.

Hypochlorous is a very weak acid. The carbonic anhydride of the air is able to expel the acid from the moist salts. The hypochlorites are almost unknown in a state of purity.

When chlorine is passed into a cold dilute solution of an alkaline hydrate, a mixture of chloride and hypochlorite is formed:

$2\mathbf{O}KH$	+	Cl_2	=	KCl	+	$ClKo$	+	$\mathbf{O}H_2$.
Potassic hydrate.				Potassic chloride.		Potassic hypochlorite.		Water.

But when the hydrate of an alkaline earth is employed, the dyad character of the metal determines the formation of a compound which is simultaneously a chloride and a hypochlorite, one of the bonds being united with chlorine and the other with chloroxyl. Thus the calcium compound (bleaching-powder) has the graphic formula Cl—Ca—O—Cl:

$\mathbf{Ca}Ho_2$	+	Cl_2	=	$\mathbf{Ca}(OCl)Cl$	+	$\mathbf{O}H_2$.
Calcic hydrate.				Bleaching-powder.		Water.

Many chemists have considered that bleaching-powder is a mixture of calcic chloride with calcic hypochlorite in molecular proportions; but the properties of the compound do not support this view. Calcic chloride is deliquescent and soluble in alcohol: whereas bleaching-powder, if properly prepared, does not deliquesce, and no calcic chloride can be extracted from it with alcohol.

By the action of the stronger acids bleaching-powder yields free chlorine:

$\mathbf{Ca}(OCl)Cl$	+	$\mathbf{S}O_2Ho_2$	=	$\mathbf{S}O_2Cao''$	+	$\mathbf{O}H_2$	+	Cl_2.
Bleaching-powder.		Sulphuric acid.		Calcic sulphate.		Water.		

CHLORIC ACID.

$$\begin{cases}\mathbf{O}Cl \\ \mathbf{O}Ho\end{cases} \text{ or } \begin{cases}\mathbf{O}Cl \\ O \\ \mathbf{O}H\end{cases}$$

Molecular weight = 84.5.

History.—This compound was discovered by Berthollet in 1786.

Preparation.—Chloric acid is prepared by the action of dilute sulphuric acid upon baric chlorate:

$$\begin{Bmatrix} \mathbf{O}Cl \\ O \\ Bao'' \\ O \\ \mathbf{O}Cl \end{Bmatrix} + SO_2Ho_2 = 2\begin{Bmatrix} \mathbf{O}Cl \\ \mathbf{O}Ho \end{Bmatrix} + SO_2Bao''.$$

Baric chlorate. Sulphuric acid. Chloric acid. Baric sulphate.

The point of complete precipitation must be exactly attained, so that no excess of either reagent is present. This may be ascertained by testing a couple of samples of the supernatant liquid—one with sulphuric acid and the other with baric chlorate. No precipitate ought to be produced in either case. The clear liquid must be decanted from the precipitate of baric sulphate, and evaporated *in vacuo* over sulphuric acid. In this way it may be concentrated till it contains 40 per cent. of chloric acid, beyond which point it decomposes.

Properties.—Thus prepared, chloric acid is a syrupy liquid of a yellowish color, possessing powerful oxidizing properties. A few drops of the acid falling upon paper produce instantaneous ignition. Sulphur and phosphorus are also inflamed by it. The dilute solution bleaches vegetable colors. It is a monobasic acid.

By boiling, it is decomposed into perchloric acid, water, chlorine, and oxygen:

$$3\begin{Bmatrix} \mathbf{O}Cl \\ \mathbf{O}Ho \end{Bmatrix} = \begin{Bmatrix} \mathbf{O}Cl \\ O \\ \mathbf{O}Ho \end{Bmatrix} + \mathbf{O}H_2 + Cl_2 + 2O_2.$$

Chloric acid. Perchloric acid. Water.

Chlorates.—Potassic chlorate may be prepared by passing an excess of chlorine into a hot concentrated solution of potassic hydrate:

$$6\mathbf{O}KH + 3Cl_2 = 5KCl + \begin{Bmatrix} \mathbf{O}Cl \\ \mathbf{O}Ko \end{Bmatrix} + 3\mathbf{O}H_2.$$

Potassic hydrate. Potassic chloride. Potassic chlorate. Water.

The chlorate is less soluble than the chloride, and separates out in tabular crystals. It may be purified by recrystallization.

Calcic chlorate is formed when chlorine is passed through boiling milk of lime:

$$6\mathbf{Ca}Ho_2 + 6Cl_2 = \begin{Bmatrix} \mathbf{O}Cl \\ O \\ Cao'' \\ O \\ \mathbf{O}Cl \end{Bmatrix} + 5\mathbf{Ca}Cl_2 + 6\mathbf{O}H_2.$$

Calcic hydrate. Calcic chlorate. Calcic chloride. Water.

By the addition of potassic chloride to the calcic chlorate, potassic chlorate is formed; the latter is then separated from the very soluble calcic chloride by crystallization:

$$\left\{\begin{array}{l}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathrm{Cao}''\\ \mathrm{O}\\ \mathbf{O}\mathrm{Cl}\end{array}\right. + 2\mathrm{KCl} = 2\left\{\begin{array}{l}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ko}\end{array}\right. + \mathbf{Ca}\mathrm{Cl}_2.$$

Calcic chlorate. Potassic chloride. Potassic chlorate. Calcic chloride.

This is the method by which potassic chlorate is prepared on a large scale.

All the chlorates are soluble in water and many are deliquescent.

The chlorates yield no precipitate with argentic nitrate; but, on ignition, they part with their oxygen, and the resulting chloride, when dissolved in water, gives with argentic nitrate a white precipitate of argentic chloride. Treated with concentrated sulphuric acid, the dry chlorates evolve a yellow gas (ClO_2).

PERCHLORIC ACID.

$$\left\{\begin{array}{l}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Ho}\end{array}\right. \text{ or } \left\{\begin{array}{l}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathrm{O}\\ \mathbf{O}\mathrm{H}\end{array}\right. .$$

Molecular weight = 100.5.

History.—Perchloric acid was discovered by Count Stadion in 1815.

Preparation.—It has already been mentioned (p. 182) that perchloric acid is formed when chloric acid is heated. The best method, however, of obtaining it consists in decomposing a perchlorate with sulphuric acid:

$$2\left\{\begin{array}{l}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Ko}\end{array}\right. + \mathbf{S}\mathrm{O_2Ho_2} = 2\left\{\begin{array}{l}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Ho}\end{array}\right. + \mathbf{S}\mathrm{O_2Ko_2}.$$

Potassic perchlorate. Sulphuric acid. Perchloric acid. Potassic sulphate.

Pure dry potassic perchlorate is distilled from a small retort with four times its weight of concentrated (previously boiled) sulphuric acid. At a temperature of 110° C. (230° F.), dense fumes are evolved and a colorless or slightly yellow liquid, consisting of pure perchloric acid, distils over. If the distillation be continued, the liquid distillate solidifies to a crystalline mass, consisting of an aquate of the formula $\left\{\begin{array}{l}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Ho}\end{array}\right., \mathbf{O}\mathrm{H_2}$. If this crystalline aquate be re-distilled, it breaks up into the pure acid, which passes over first, and an aqueous acid boiling at 203° C. (397° F.) (Roscoe).

Properties.—Pure perchloric acid is a colorless volatile liquid with a specific gravity of 1.782 at 15.5° C. (59.9° F.). It fumes strongly in

contact with moist air. It is one of the most powerful oxidizing agents known: brought in contact with organic substances, it causes them to inflame with explosive violence. A few drops, falling upon charcoal, produce ignition and explosion. In contact with the skin, it causes dangerous wounds which do not heal for months. The pure acid cannot be re-distilled without decomposition: the liquid in the retort becomes gradually darker in color, and ultimately explodes. Perchloric acid decomposes spontaneously at ordinary temperatures, and sealed glass tubes containing this substance burst from the internal pressure even when kept in the dark.

Aqueous perchloric acid reddens litmus, but does not bleach. Unlike the other oxygen acids of chlorine, it is not reduced, in a diluted state, by sulphurous anhydride or sulphuretted hydrogen.

Preparation of Potassic Perchlorate.—1. When potassic chlorate is heated, it fuses and gives off oxygen, but after a short time the fused mass becomes pasty and the evolution of gas ceases. In order to expel the remainder of the oxygen, a much higher temperature is necessary. If the operation be interrupted at the end of this first stage, it will be found that only one-third of the total oxygen from the chlorate has been expelled, and that the fused mass in the retort contains, along with potassic chloride, a new salt, potassic perchlorate:

$$2\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ko}\end{matrix}\right. = \mathrm{KCl} + \left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Ko}\end{matrix}\right. + \mathrm{O_2}.$$

Potassic chlorate. — Potassic chloride. — Potassic perchloride.

The fused mass is powdered and treated with water to remove the potassic chloride. The undissolved residue is digested with warm hydrochloric acid so long as chlorine or its oxides are evolved, and in this way any unaltered chlorate is converted into chloride. A final washing with water removes the chloride, leaving the perchlorate in a state of purity.

2. When potassic chlorate is gradually added to boiling nitric acid, chlorine and oxygen are evolved, whilst potassic nitrate and perchlorate are formed:

$$3\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ko}\end{matrix}\right. + 2\mathrm{N}\mathbf{O}_2\mathrm{Ho} = 2\mathrm{N}\mathbf{O}_2\mathrm{Ko} + \mathbf{O}\mathrm{H_2} + \left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Ko}\end{matrix}\right. + \mathrm{Cl_2} + 2\mathrm{O_2}.$$

Potassic chlorate. — Nitric acid. — Potassic nitrate. — Water. — Potassic perchlorate.

These salts are then separated by crystallization.

Potassic perchlorate is soluble in 65 parts of water at 15° C. (59° F.).

The perchlorates are all soluble in water, and some of them are deliquescent. They require a higher temperature for their decomposition than the chlorates; they are not attacked by hydrochloric acid, and do not yield chloric peroxide when heated with concentrated sulphuric acid.

CHAPTER XXIV.

TRIAD ELEMENTS.

SECTION I.

BORON, B_2.

Atomic weight = 11. *Probable molecular weight* = 22. *Sp. gr., adamantine variety*, 2.68. *Atomicity* ‴. *Evidence of atomicity:*

Boric chloride, ...	$\mathbf{B}'''Cl_3$.
Boric fluoride, ...	$\mathbf{B}'''F_3$.
Boric ethide, ...	$\mathbf{B}'''Et_3$.

History.—Boron was first prepared from boric anhydride by Gay-Lussac and Thenard in 1808, and immediately afterwards independently by Davy.

Occurrence.—Boron is found only in combination with oxygen, either as free boric acid, or united with various bases to form borates. Of these last, the commonest is *borax* or *tincal*, a sodic borate.

Preparation:

a. Amorphous Boron.—1. This variety may be obtained by heating boric anhydride with sodium:

$$\underset{\text{Boric anhydride.}}{\mathbf{B}_2O_3} + 3Na_2 = \underset{\text{Sodic oxide.}}{3\mathbf{O}Na_2} + B_2.$$

After the reaction, which is somewhat violent, has ceased, the fused mass is allowed to cool, and is then dissolved in dilute hydrochloric acid. The boron remains behind as a fine brown powder.

2. Another method consists in passing the vapor of boric chloride over heated potassium:

$$\underset{\text{Boric chloride.}}{2\mathbf{B}Cl_3} + 3K_2 = \underset{\text{Potassic chloride.}}{6KCl} + B_2.$$

β. Adamantine Boron.—On fusing boric anhydride with aluminium, the boric anhydride is reduced:

$$Al_2 + \underset{\text{Boric anhydride.}}{\mathbf{B}_2O_3} = \underset{\text{Aluminic oxide.}}{(\mathbf{Al}''')_2O_3} + B_2.$$

The boron thus formed dissolves in the molten aluminium, and on cooling is deposited in crystals in the interior of the mass. The aluminium is dissolved in caustic soda, leaving the crystals of diamond boron (Wöhler and Deville).

The so-called *graphitoid boron*, which is formed in laminæ during the preparation of adamantine boron, is a definite compound of boron and aluminium, of the formula Al_2B_6.

Properties.—Amorphous boron is a brown powder, infusible at a white heat in an atmosphere of a gas which is without chemical action upon it, but fusible in the electric arc.

Adamantine or diamond boron forms transparent octahedral crystals which vary in color from an almost imperceptible honey-yellow to a deep garnet-red, and possess a lustre and refractive power almost equal to those of the diamond. In hardness it lies between corundum and diamond. Its specific gravity is 2.68.

Adamantine boron is, strictly speaking, not a pure variety of boron. The crystals always contain a small quantity of aluminium and, in cases where the crucible has been lined with charcoal in their preparation, also carbon (Hampe, *Liebig's Annalen*, **183**, 75).

A pure adamantine boron is stated to have been obtained by fusing amorphous boron with silver.

Reactions.—1. When amorphous boron is heated in air, it burns, forming boric anhydride, which fuses, coating the boron and preserving it from further oxidation.

2. Amorphous boron decomposes hot sulphuric acid:

$$B_2 + \underset{\text{Sulphuric acid.}}{3\mathbf{S}O_2Ho_2} = \underset{\text{Boric anhydride.}}{\mathbf{B}_2O_3} + \underset{\text{Water.}}{3\mathbf{O}H_2} + \underset{\text{Sulphurous anhydride.}}{3\mathbf{S}O_2}.$$

3. Nitric acid, even when only slightly concentrated, attacks it in the cold:

$$B_2 + \underset{\text{Nitric acid.}}{6\mathbf{N}O_2Ho} = \underset{\text{Boric acid.}}{2\mathbf{B}Ho_3} + \underset{\text{Nitric peroxide.}}{3'\mathbf{N}^{iv}{}_2O_4}.$$

4. At a red heat it decomposes alkaline carbonates, sulphates, and nitrates, forming borates:

$$B_2 + \underset{\text{Sodic carbonate.}}{3\mathbf{C}ONao_2} = \underset{\text{Trisodic borate.}}{2\mathbf{B}Nao_3} + \underset{\text{Carbonic oxide.}}{3\mathbf{C}''O}.$$

$$B_2 + \underset{\text{Potassic sulphate.}}{3\mathbf{S}O_2Ko_2} = \underset{\text{Tripotassic borate.}}{2\mathbf{B}Ko_3} + \underset{\text{Sulphurous anhydride.}}{3\mathbf{S}O_2}.$$

$$B_2 + \underset{\text{Potassic nitrate.}}{6\mathbf{N}O_2Ko} = \underset{\text{Tripotassic borate.}}{2\mathbf{B}Ko_3} + \underset{\text{Nitric peroxide.}}{3'\mathbf{N}^{iv}{}_2O_4}.$$

5. Fused with potassic hydrate it forms a borate, with evolution of hydrogen:

$$B_2 + \underset{\text{Potassic hydrate.}}{6\mathbf{O}KH} = \underset{\text{Potassic borate.}}{2\mathbf{B}Ko_3} + 3H_2.$$

6. It is one of the very few elements which unite directly with

nitrogen. When strongly heated in a current of this gas, it is converted into white boric nitride:

$$\underset{}{B_2} + N_2 = \underset{\text{Boric nitride.}}{2BN'''}.$$

This compound is, however, best prepared by heating to bright redness a mixture of 1 part of anhydrous borax with 2 parts of ammonic chloride. The boric nitride is thus obtained as a white amorphous powder. It is a very stable substance, and is only slowly acted upon by boiling solutions of alkalies or acids. Fused with caustic potash, it forms potassic borate with evolution of ammonia:

$$\underset{\text{Boric nitride.}}{BN'''} + \underset{\text{Potassic hydrate.}}{3OKH} = \underset{\text{Potassic borate.}}{BKo_3} + \underset{\text{Ammonia.}}{NH_3}.$$

When heated in a current of steam, the nitride is decomposed in a similar manner, yielding boric acid and ammonia.

Adamantine boron is much less easily attacked by heat and by reagents than the amorphous variety. It does not fuse in the flame of the oxy-hydrogen blowpipe. Heated in oxygen to the temperature of combustion of the diamond, it undergoes only superficial oxidation; but it enflames at a red heat in chlorine, and is converted into boric chloride. Acids do not attack it at any temperature; but when fused with hydric potassic sulphate, boric anhydride is formed:

$$\underset{\text{Hydric potassic sulphate.}}{6SO_2HoKo} + B_2 = \underset{\text{Boric anhydride.}}{B_2O_3} + \underset{\text{Potassic sulphate.}}{3SO_2Ko_2} + \underset{\text{Water.}}{3OH_2} + \underset{\text{Sulphurous anhydride.}}{3SO_2}.$$

COMPOUND OF BORON WITH HYDROGEN.

BORIC HYDRIDE.

BH_3?

Preparation.—This compound is obtained, mixed with a very large excess of hydrogen, by the action of hydrochloric acid upon magnesic boride (F. Jones):

$$\underset{\text{Magnesic boride.}}{B_2Mg_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Boric hydride.}}{2BH_3} + \underset{\text{Magnesic chloride.}}{3MgCl_2}.$$

The magnesic boride is prepared by heating boric anhydride with magnesium filings.

Properties.—Boric hydride is a colorless gas with a characteristic odor. It produces nausea and headache when inhaled, even in moderate quantity. It is sparingly soluble in water, to which it imparts its odor.

Reactions.—1. Boric hydride burns with a green flame, producing boric anhydride and water:

$$\underset{\text{Boric hydride.}}{2BH_3} + 3O_2 = \underset{\text{Boric anhydride.}}{B_2O_3} + \underset{\text{Water.}}{3OH_2}.$$

2. Burnt with an insufficient supply of air, it yields water and free boron:

$$\underset{\text{Boric hydride.}}{2BH_3} + 3O = B_2 + \underset{\text{Water.}}{3OH_2}.$$

This may be shown by holding a cold surface of white porcelain in the flame, when a brown film of boron is deposited.

3. When passed through a red-hot tube it is decomposed into its elements, and the boron is deposited as a brown film beyond the heated portion of the tube.

4. It combines with ammonia to form a compound of unknown composition.

5. From a solution of argentic nitrate it throws down a black precipitate containing both silver and boron.

*COMPOUNDS OF BORON WITH THE HALOGENS.**

BORIC CHLORIDE.

BCl_3.

Molecular weight = 117.5. *Molecular volume* $\Box\Box$. 1 *litre of boric chloride vapor weighs* 58.75 *criths. Sp. gr.* 1.35 *at* 17° C. (52.6° F.). *Boils at* 18.23° C. (64.81° F.).

Preparation.—1. Amorphous boron spontaneously inflames in chlorine forming boric chloride. In the case of the crystalline modification, it is necessary to heat the boron in order to induce combination.

2. Boric chloride is best prepared by the action of chlorine on a mixture of boric anhydride and charcoal heated to redness:

$$\underset{\text{Boric anhydride.}}{B_2O_3} + 3Cl_2 + 3C = \underset{\text{Boric chloride.}}{2BCl_3} + \underset{\text{Carbonic oxide.}}{3CO}.$$

The mixture of boric anhydride and charcoal is contained in a porcelain tube heated in a furnace. The gaseous boric chloride passes through a Y-shaped tube immersed in a freezing-mixture, where it condenses, and drops through the lower limb of the tube into a flask beneath, which is also surrounded by a freezing-mixture. The boric chloride may be freed from excess of chlorine by digestion with mercury.

* *Halogens*, "salt producers" (from ἅλς, salt; and γεννάω, I bring forth), is a collective name for the four elements chlorine, bromine, iodine, and fluorine.

The above process is one frequently employed for obtaining chlorides of elements from their oxides. The chlorine alone cannot separate the boron from the oxygen, nor can the carbon alone detach the oxygen from the boron; but by the united action of the chlorine and the carbon this decomposition is effected.

Properties.—Boric chloride is a colorless, very mobile, strongly refracting liquid, boiling at 18.23° C. (64.81° F.). Its specific gravity at 17° C. is 1.35. When heated it expands very rapidly. It fumes in the air, and is decomposed by water with formation of hydrochloric and boric acids:

$$\underset{\text{Boric chloride.}}{BCl_3} + \underset{\text{Water.}}{3OH_2} = \underset{\text{Hydrochloric acid.}}{3HCl} + \underset{\text{Boric acid.}}{BHo_3}.$$

With gaseous ammonia it yields a molecular compound $3NH_3,2BCl_3$, which forms a white crystalline powder.

BORIC BROMIDE.

BBr_3.

Molecular weight = 251. *Molecular volume* ☐☐. 1 *litre of boric bromide vapor weighs* 125.5 *criths.* *Sp. gr. of liquid* = 2.69. *Boils at* 90° C.

This compound is prepared by passing bromine vapor over a red-hot mixture of boric anhydride and charcoal in a manner similar to that described under the preparation of boric chloride. It is purified by rectification from mercury, and forms a colorless mobile liquid.

Its reactions and decompositions resemble those of boric chloride.

BORIC FLUORIDE.

BF_3.

Molecular weight = 68. *Molecular volume* ☐☐. 1 *litre weighs* 34 *criths.*

History.—Boric fluoride was discovered by Gay-Lussac and Thenard in 1808.

Preparation.—1. If a mixture of 2 parts of fluorspar and 1 part of boric anhydride, both thoroughly dried, be heated to redness in an iron retort, boric fluoride is evolved as a colorless gas, and may be collected over mercury:

$$\underset{\text{Boric anhydride.}}{2B_2O_3} + \underset{\text{Calcic fluoride.}}{3CaF_2} = \underset{\text{Calcic borate.}}{B_2Cao''_3} + \underset{\text{Boric fluoride.}}{2BF_3}.$$

2. A better method consists in heating together in a flask 2 parts of fluorspar, 1 part of boric anhydride, and 12 parts of sulphuric acid:

$$\underset{\text{Boric anhydride.}}{B_2O_3} + \underset{\text{Calcic fluoride.}}{3CaF_2} + \underset{\text{Sulphuric acid.}}{3SO_2Ho_2} = \underset{\text{Dihydric calcic sulphate.}}{3SOHo_2Cao''} + \underset{\text{Boric fluoride.}}{2BF_3}.$$

Properties.—Boric fluoride is a colorless gas, possessing a very pungent odor. Its vapor density (air = 1) is 2.312. Water absorbs 700

times its volume of the gas. Its great affinity for water causes it to fume strongly in the air. A piece of dry paper introduced into the gas is charred by the abstraction of the elements of water from the cellulose.

It combines with gaseous ammonia to form three distinct compounds, BF_3,NH_3,—$BF_3,2NH_3$,—and $BF_3,3NH_3$. The first is a white solid; the others are colorless liquids. The two last evolve ammonia on heating, and are converted into the solid compound.

Hydrofluoboric Acid.—By the action of water on boric fluoride, hydrofluoboric acid (BF_3,HF) is formed:

$$\underset{\text{Boric fluoride.}}{4BF_3} + \underset{\text{Water.}}{3OH_2} = \underset{\text{Hydrofluoboric acid.}}{3(BF_3,HF)} + \underset{\text{Boric acid.}}{BHo_3}.$$

The solution obtained by saturating water with boric fluoride is an oily fuming liquid with a specific gravity of 1.77. It chars organic bodies.

Hydrofluoboric acid acts upon metallic hydrates, forming salts known as *borofluorides:*

$$\underset{\text{Hydrofluoboric acid.}}{BF_3,HF} + \underset{\text{Potassic hydrate.}}{OKH} = \underset{\text{Potassic borofluoride.}}{BF_3,KF} + \underset{\text{Water.}}{OH_2}.$$

Possibly the boron in these compounds is pentadic; thus B^vF_4H and B^vF_4K.

COMPOUNDS OF BORON WITH OXYGEN AND HYDROXYL.

Boric anhydride, ...	B_2O_3.
Monobasic boric acid, Metaboric acid, ...	$BOHo$.
Tribasic boric acid, Boric acid, ...	BHo_3.

BORIC ANHYDRIDE, *Boracic anhydride.*

B_2O_3.

Molecular weight = 70. *Sp. gr.* 1.83.

Preparation.—Boric anhydride is obtained by heating boric acid to redness:

$$\underset{\text{Boric acid.}}{2BHo_3} = \underset{\text{Boric anhydride.}}{B_2O_3} + \underset{\text{Water.}}{3OH_2}.$$

Properties.—Freshly prepared boric anhydride is a colorless transparent vitreous solid, which, however, when exposed to the air gradually absorbs moisture and becomes opaque. When fused at a red heat, it forms a viscous liquid like melted glass. At a white heat it volatil-

izes. Although boric acid is one of the weakest acids, the non-volatility of its anhydride at any but the highest temperatures enables it to expel stronger volatile acids from their salts when heated with them. The sulphates are converted into borates with evolution of sulphuric anhydride:

$$\underset{\text{Sodic sulphate.}}{3\mathbf{S}O_2Nao_2} + \underset{\text{Boric anhydride.}}{\mathbf{B}_2O_3} = \underset{\text{Sodic borate.}}{2\mathbf{B}Nao_3} + \underset{\text{Sulphuric anhydride.}}{3\mathbf{S}O_3}.$$

Boric anhydride dissolves most metallic oxides when fused with them, yielding in many cases characteristically colored glasses—a property which has led to its employment as a blowpipe reagent. By gradually volatilizing at a white heat the boric anhydride in which a metallic oxide is dissolved, the latter may frequently be obtained in a crystallized form, and in this way many minerals have been artificially produced. Alumina crystallizes from this solvent in the hexagonal forms of corundum, and a mixture of alumina and magnesia yields octahedral crystals of spinelle. These artificial products are identical in all their physical and chemical properties with the natural minerals.

BORIC ACID, *Boracic acid, Orthoboric acid.*

$\mathbf{B}Ho_3$.

Molecular weight = 62. *Sp. gr.* 1.479.

Occurrence.—In some parts of the volcanic districts of Tuscany, jets of gas or steam, known as *soffioni* or *fumaroles*, escape through fissures in the ground. This steam contains traces of boric acid. Round the soffioni pools of water, called *lagoons*, have collected, into which the steam passes, and in these the boric acid accumulates.

The method of extracting the acid is as follows:—Above the *soffioni*, cisterns of glazed masonry are constructed, so that the vapors from two or more soffioni pass into each cistern. The highest cistern is filled by temporarily directing the waters of a stream into it. At the end of twenty-four hours the water from this first cistern, having taken up a certain quantity of boric acid, is run off into a lower cistern, and its place is supplied by fresh water. The water remains in the second cistern for twenty-four hours, and is then run into a third cistern. This treatment is continued till the water has passed through six or seven cisterns, when it contains about 2 per cent of boric acid. It is then transferred to tanks, where it remains for twenty-four hours in order to allow the suspended earthy impurities to settle. The clear liquid is then allowed to run in a thin stream over a long roof of corrugated sheet lead, heated from beneath by the steam of a *soffione.* In this way a considerable concentration is effected. The liquid is finally evaporated in pans to the crystallizing point. The crude substance thus obtained is recrystallized from boiling water. The crystals are placed in wicker baskets to drain, and afterwards dried in a kiln which is heated by the steam of a *soffione.* The lagoons of Tuscany

yield about 750,000 kilograms of boric acid yearly. Artificial *soffioni* are now produced by boring.

Salts of boric acid also occur in nature. The mineral *tincal,* or natural borax, an abnormal sodic borate of the formula

$$\mathbf{B}_4O_5Nao_2,10\mathbf{O}H_2,$$

is found in Thibet.

Preparation.—Boric acid may be obtained by the action of hydrochloric acid on borax:

$$\underset{\text{Borax.}}{\mathbf{B}_4O_5Nao_2} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Water.}}{5\mathbf{O}H_2} = \underset{\text{Boric acid.}}{4\mathbf{B}Ho_3} + \underset{\text{Sodic chloride.}}{2NaCl.}$$

One part of borax is dissolved in $2\frac{1}{2}$ parts of boiling water and an excess of concentrated hydrochloric acid is added. On cooling, the boric acid crystallizes out in thin plates.

For laboratory purposes boric acid is best prepared by recrystallization of the commercial acid.

Properties.—Boric acid, as crystallized from water, forms lustrous laminæ, unctuous to the touch. One hundred parts of water at 10° C. dissolve 2 parts, at 100° C., 8 parts, of boric acid. The solution turns blue litmus wine-red, and turmeric paper, even in presence of hydrochloric acid, brown. When the aqueous solution is boiled, the boric acid volatilizes with the steam, as in the *soffioni.* Boric acid is also slightly soluble in alcohol, and communicates to the flame of the alcohol a characteristic green coloration.

At a temperature of 100° C., boric acid parts with the elements of water, and is converted into metaboric acid, $\mathbf{B}OHo$:

$$\underset{\text{Boric acid.}}{\mathbf{B}Ho_3} = \underset{\text{Metaboric acid.}}{\mathbf{B}OHo} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

Metaboric acid forms stable salts, such as sodic metaborate ($\mathbf{B}ONao$) and magnesic metaborate $\left(\begin{cases}\mathbf{B}O \\ Mgo'' \\ \mathbf{B}O\end{cases}\right)$.

When boric acid is heated for a long time to 140° C. (284° F.) tetraboric acid is formed as a brittle vitreous mass:

$$\underset{\text{Boric acid.}}{4\mathbf{B}Ho_3} = \underset{\text{Tetraboric acid.}}{\mathbf{B}_4O_5Ho_2} + \underset{\text{Water.}}{5\mathbf{O}H_2.}$$

The tetraborates are also stable compounds. Anhydrous borax ($\mathbf{B}_4O_5Nao_2$) is sodic tetraborate.

The normal borates or orthoborates, derived from the tribasic acid ($\mathbf{B}Ho_3$), are the least stable of the compounds of boric acid.

BORIC SULPHIDE.

$B_2S''_3$.

Molecular weight = 118.

Preparation.—Boric sulphide is formed when the vapor of sulphur is passed over heated boron; but it is best prepared by heating to bright redness a mixture of lamp-black and boric anhydride in a current of carbonic disulphide vapor:

$$\underset{\text{Boric anhydride.}}{2B_2O_3} + \underset{\text{Carbonic disulphide.}}{3CS''_2} + 3C = \underset{\text{Boric sulphide.}}{2B_2S''_3} + \underset{\text{Carbonic oxide.}}{6C''O}.$$

Properties.—Boric sulphide is thus obtained as a solid, yellowish-white, fusible, vitreous mass, which may be volatilized in a current of sulphuretted hydrogen, and then forms silky needles. It has a pungent odor, and its vapor irritates the eyes. Water at once decomposes it into sulphuretted hydrogen and boric acid:

$$\underset{\text{Boric sulphide.}}{B_2S''_3} + \underset{\text{Water.}}{6OH_2} = \underset{\text{Sulphuretted hydrogen.}}{3SH_2} + \underset{\text{Boric acid.}}{2BHo_3}.$$

CHAPTER XXV.

TETRAD ELEMENTS.

SECTION I.

CARBON, C.

Atomic weight = 12. *Atomicity* $''$ *and* ^{iv}. *Evidence of atomicity:*

Carbonic oxide, ...	$C''O$.
Carbonic tetrachloride, ...	$C^{iv}Cl_4$.
Marsh-gas, ...	$C^{iv}H_4$.
Chloroform, ...	$C^{iv}HCl_3$

Occurrence.—Carbon exists in the free state in three distinct allotropic modifications, as amorphous carbon, as graphite, and as diamond, all of which are found in nature. In combination with oxygen as carbonic anhydride, it occurs in the air. It is a constituent of all organic substances, and upon its varied combining powers the infinite manifoldness of the animal and vegetable kingdoms ultimately depends.

General Properties.—The following properties are common to carbon in all its modifications: It is solid, infusible, probably non-volatile at the highest temperatures that can be artificially produced, and insoluble in all known solvents at ordinary temperatures.

a. Amorphous Carbon.—The chief varieties of amorphous carbon are: Charcoal, lamp-black, gas-carbon, and coke.

Occurrence.—Amorphous carbon is found in nature as mineral charcoal.

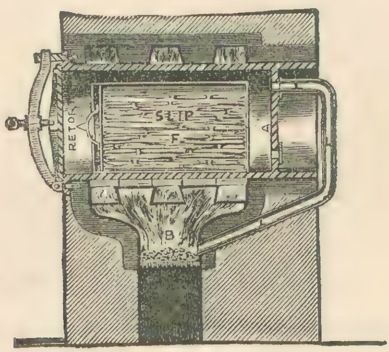
Charcoal.

Preparation.—When wood is heated to redness in closed vessels, the cellulose $(C_6H_{10}O_5)_x$ gives off its oxygen and hydrogen, partly as water, partly along with a portion of the carbon in the form of oxides of carbon and of more or less complex organic compounds. When these various gaseous and liquid products of destructive distillation have ceased to be evolved, the charcoal remains behind in the retort as a black, non-lustrous substance, preserving the form of the wood from which it was prepared. The liquid products of distillation constitute wood-tar, and their nature will be described under Organic Chemistry.

In order to obtain the greatest possible yield of charcoal, care must be taken to expel all moisture from the wood before raising the temperature to redness, otherwise the charcoal at a red heat will decompose the water, forming carbonic anhydride or carbonic oxide and liberating hydrogen.

The distillation is performed in cast-iron retorts. The wood to be carbonized is placed in a perforated iron case F (Fig. 31), known as a *slip*, which is then introduced into the retort A. The volatile products

FIG. 31.



of decomposition are led by the pipe L into the furnace B, where they are burned, a saving of fuel thus being effected. In well-arranged works at the present day, these products are condensed, acetic acid and wood-naphtha being obtained from them. One hundred parts of wood yield on an average 27 parts of charcoal.

In countries where wood is plentiful, a method of carbonizing in heaps is employed, the heat being produced by the combustion of a part of the wood. This is the oldest process of charcoal-burning. The logs are piled on end in a heap (Fig. 32), and a space is left in the middle to serve as a flue. The whole is covered with turf and earth, small apertures being made at the base of the heap to admit air. Fire is applied from below, and the action of the heat is carefully regulated by opening or closing the air-holes in different parts of the heap. The charcoal obtained by this method is inferior in quality to that produced by carbonizing in retorts.

A very pure charcoal for special laboratory purposes is obtained by carbonizing sugar in a closed platinum vessel. If it is necessary to get

rid of the last traces of hydrogen, the product must be strongly ignited in a current of chlorine. This charcoal possesses the advantage of containing no silica, and may therefore be employed in the preparation of volatile chlorides (see *boric chloride*, p. 188), which would otherwise be contaminated with silicic chloride (**Si**Cl_4).

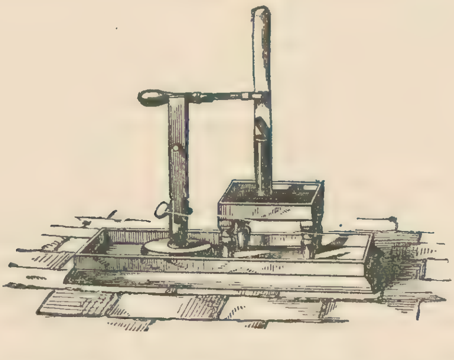
Another variety of charcoal is *animal charcoal* or *bone-black*, produced by the carbonization of bones in closed vessels. A fetid oil of very complex character distils over during the process. The charred mass which remains in the retort is afterwards coarsely granulated, in

Fig. 32.

which form it is employed to decolorize liquids. Animal charcoal which has lost its decolorizing properties by repeated use may have these restored by again heating it in closed vessels. A very pure animal charcoal is obtained by carbonizing dried blood which has been mixed with potassic carbonate, in order to render the product more porous. The potash is afterwards extracted with hydrochloric acid.

Properties.—The qualities of the product vary with the temperature employed. The best wood-charcoal for laboratory and metallurgical purposes is prepared at a high temperature, and is a hard brittle sub-

Fig. 33.



stance with a lustrous fracture. When struck, it emits a metallic sound. Common charcoal is a bad conductor of heat and electricity; but by exposing it for a long time in closed vessels to a very high temperature, it becomes an excellent conductor.

The elimination of the oxygen and hydrogen from the wood in the formation of charcoal leaves the mass in an extremely porous condition,

and the infusibility of the charcoal causes it to retain this porosity. A very small piece of charcoal may thus expose an enormous surface, and hence all phenomena dependent upon surface action are displayed in a high degree by this substance. To this class belong the condensation of gases and decolorizing of liquids.

The absorbent power of wood-charcoal for gases may be shown by cooling a fragment of freshly ignited charcoal under mercury, and then passing it into a tube filled with gaseous ammonia over the mercurial trough (Fig. 33). The mercury will rapidly rise in the tube as the ammonia is absorbed. The following list gives the volumes of some of the principal gases absorbed by one volume of boxwood-charcoal at 0° C., and under a pressure of 760 mm., as determined by Hunter:

Absorption of gases by charcoal—

	Vols.
Hydrogen,	4.4
Nitrogen,	15.2
Oxygen,	17.9
Carbonic oxide,	21.2
Carbonic anhydride,	67.7
Nitric oxide,	70.5
Nitrous oxide,	86.3
Ammonia,	171.7

As a rule the most easily liquefiable gases are absorbed in greatest quantity by charcoal.

Noxious effluvia are in like manner absorbed by charcoal, and at the same time undergo oxidation at the expense of the oxygen condensed in its pores, a property which has led to the use of charcoal for disinfecting purposes.

The property of decolorizing liquids depends upon the absorption of the coloring matter in the pores of the charcoal. Animal charcoal is best suited for this purpose, inasmuch as the inorganic matter contained in the bones increases the porosity of the product. If a red wine be warmed with freshly ignited animal charcoal and then filtered, the filtrate will be colorless. In the process of sugar refining the raw syrup is decolorized by filtration through animal charcoal. Charcoal filters are also employed for the purification of water for drinking purposes, but they are not to be recommended, owing to the stimulus which animal charcoal gives to the development of animalcular life.

Lamp-black.—When certain organic substances rich in carbon, such as resins, essential oils, and heavy hydrocarbons, are burned in air, the supply of oxygen is insufficient for complete combustion, and the flame smokes. A porcelain dish or any cold object held in the flame is quickly covered with a finely divided black deposit. This is the substance known as *lamp-black.*

On a large scale, the tar, resin, or other highly carbonaceous substance is burnt with a limited supply of air, and the heavy smoke is made to pass through chambers, where the lamp-black settles.

Lamp-black, after strong ignition in a stream of chlorine in order to

free it from the hydrogen which the ordinary product always contains, is one of the purest forms of amorphous carbon.

Lamp-black is employed in the manufacture of printing ink and China ink, and also as a common black paint.

Coke.—When coal is subjected to destructive distillation in the manufacture of coal-gas, a number of volatile products are expelled, and an impure amorphous carbon, known as *coke*, remains in the retort. Coke is also prepared by burning coal in heaps, as in the conversion of wood into charcoal; but in the coking-heap the central flue is built of fire-bricks. The coking is thus effected by the combustion of a portion of the coal. As soon as smoke ceases to be given off, the air-holes at the bottom of the heap are closed with wet sand, or, more frequently, the fire is quenched with water. At the present day most of the coke is obtained by partially burning the coal in specially constructed coking ovens. The coke prepared in ovens is denser and of better quality than that obtained by other means. Coke does not ignite readily, nor is its combustion well maintained, except in large masses and with the aid of a rapid current of air; but its combustion produces a very high temperature, and is unattended with the production of smoke. It is largely used in iron smelting and other metallurgical operations.

Gas Carbon.—This substance is also produced in the manufacture of coal-gas. When the heavier hydrocarbons formed from the coal pass over the red-hot walls of the retort, they deposit a portion of their carbon in an exceedingly dense and coherent form. The gas carbon so obtained forms a gray, very hard mass, possessing a metallic lustre. It is an excellent conductor of heat and electricity. The carbon-plates of the Bunsen battery, and sometimes the carbon-rods for the electric arc-light, are made from this material.

A very pure form of amorphous carbon is obtained by the action of potassium at a high temperature on carbonic anhydride or a carbonate:

$$\underset{\text{Carbonic anhydride.}}{3\mathbf{C}O_2} + 2K_2 = C + \underset{\text{Potassic carbonate.}}{2\mathbf{C}OKo_2}.$$

The carbon must be carefully washed with hydrochloric acid to free it from the last traces of alkali.

Reaction.—By treatment with a mixture of potassic chlorate and fuming nitric acid, amorphous carbon is converted into brown compounds soluble in water. Potassic permanganate, in alkaline solution, or nascent electrolytic oxygen, converts it into mellitic acid, $'''\mathbf{C}'_6(COHo)_6$, and other products.

Coal.—This substance consists of the remains of a former flora. It is the result of a decomposition which woody fibre has undergone during long geological periods under varying conditions of temperature and moisture, and with exclusion of air. Under these circumstances the hydrogen and oxygen of the wood have been gradually reduced in quantity by elimination, partly as water and partly in combination with a portion of the carbon as methylic hydride (the *fire-damp* of the miner) and carbonic anhydride. The process is thus very similar to that which occurs when wood is converted into charcoal by heating in closed

vessels. The degree of change which the woody fibre has undergone varies with the age of the coal: thus lignite, a more recent formation, preserves its fibrous structure and contains a large percentage of oxygen and hydrogen; whereas anthracite, which is found in the oldest carboniferous deposits, is dense and amorphous, and contains a very high percentage of carbon.

The following is a list of some of the chief varieties of coal:

Lignite or Brown Coal is generally of more recent date than the chalk formation; whilst true coal is older than the chalk. Its specific gravity is also lower than that of true coal. It yields a powdery coke and burns with a comparatively smokeless flame.

Bituminous or Caking Coal.—The greater number of English coals belong to this class. Bituminous coal fuses and *cakes* together on heating, giving off much smoke and gas, and yielding a lustrous coke. *Cannel coal* is a variety of bituminous coal. It contains a large percentage of hydrogen, and is much in request for purposes of gas manufacture.

Anthracite.—This is a very hard coal with a conchoidal fracture. It is of an iron-black color, with a semi-metallic lustre, and its smooth surface frequently displays iridescence. It splinters when heated, and ignites with difficulty, burning with very little flame and no smoke, and giving out an intense heat. It is much used as a steam coal and also for smelting purposes.

The following table shows the average composition of coals from different localities in Great Britain. The last column contains the thermal effect as measured by the number of pounds of water at 100° C. which were found to be converted into steam in a Cornish boiler by 1 pound of the coal:

Table showing the Average Composition of Coals from different Localities.

Locality.	Sp. gr.	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.	Ash.	Percentage of coke left by each coal.	Evaporating power
Wales, . .	1.315	83.78	4.79	0.98	1.43	4.15	4.91	72.60	9.05
Durham, .	1.256	82.12	5.31	1.35	1.24	5.69	3.77	60.67	8.37
Lancashire,	1.273	77.90	5.32	1.30	1.44	9.53	4.88	60.22	7.94
Scotland, .	1.259	78.53	5.61	1.00	1.11	9.69	4.03	54.22	7.70
Derbyshire,	1.292	79.68	4.94	1.41	1.01	10.28	2.65	59.32	7.58

β. Graphite.

Occurrence.—This variety of carbon constitutes the mineral *plumbago* or *black-lead.* It is found in various crystalline rocks, such as granite, gneiss, and piorite. It is possibly of vegetable origin, and in this case corresponds to the most complete transformation of vegetable substance, inasmuch as it never contains more than traces of hydrogen. The geological formations in which it occurs are likewise much older than the carboniferous strata.

Preparation.—1. When the diamond is exposed to the heat of the electric arc in an atmosphere devoid of oxygen, it swells up and is

converted into a black mass of graphite. The various forms of amorphous carbon are also converted into graphite under these conditions.

2. Cast iron is a compound of carbon and iron. In the molten state the iron dissolves more carbon than is required for combination, and, on cooling, this excess separates out as crystalline scales of graphite. When gray pig-iron is dissolved in an acid, the graphite remains behind.

Properties.—Graphite crystallizes in six-sided plates, in which form it sometimes occurs in nature; but it is more frequently found in granular, foliated, or fibrous masses. The natural variety is grayish-black, with a metallic lustre (hence the name *black-lead*), and is unctuous to the touch. Its specific gravity varies from 1.8 to 2.4. It is soft enough to leave a mark on paper, a property which is turned to account in the manufacture of black-lead pencils. It conducts heat and electricity well.

Reaction.—If 1 part of pure graphite be heated for some days on a water-bath to 60° with 3 parts of potassic chlorate and sufficient concentrated nitric acid to render the whole fluid, a portion of the graphite is converted into *graphitic acid* ($C_{11}H_4O_5$), and by the repetition of this treatment pure graphitic acid may be obtained in thin yellowish transparent crystals (Brodie). When heated, graphitic acid decomposes with violence, evolving gas, and yielding a very bulky finely-divided black powder of *pyrographitic oxide* ($C_{22}H_2O_4$) which is dissolved by a mixture of potassic chlorate and nitric acid. Baric graphitate detonates violently when heated.

Applications.—Graphite is chiefly employed in the manufacture of black-lead pencils. Other uses are: the coating of iron-work as a preservative against rust, the polishing of gunpowder, the lubrication of machinery, and the preparation of plumbago crucibles.

γ. Diamond.

Occurrence.—This gem is found in alluvial deposits produced by the disintegration of a particular micaceous rock known as *itacolumite.* It has also been found in matrix in the rock itself. The principal diamond fields are those of Brazil and the Cape of Good Hope.

Among all the known allotropic modifications of the elements, the diamond is remarkable as the only one which has not been produced artificially.

Properties.—The diamond crystallizes in forms derived from the regular octahedron. The faces of the crystals are very frequently convex. The finer specimens are transparent and colorless. Colored varieties are not uncommon. It possesses a characteristic and brilliant lustre, known as the *adamantine* lustre, which is due to its very high refractive and dispersive power. This lustre is artificially intensified by cutting. The diamond is the hardest of known substances, and can be cut only by means of its own dust, the gem being pressed against a revolving steel plate covered with diamond-dust and oil. Its specific gravity is 3.55. It is a non-conductor of electricity.

In closed vessels, it may be heated to very high temperatures without undergoing change, but when subjected to the heat of the electric arc it is converted into graphite. When intensely heated in air or

oxygen it burns, forming carbonic anhydride, and leaving a small quantity of ash. The diamond contains neither hydrogen nor oxygen.

The diamond is not attacked by a mixture of potassic chlorate and nitric acid.

Unlike boron and silicon, the diamond does not dissolve in molten aluminium.

Applications.—Besides its well-known use as an ornament, the diamond is employed in the arts. Diamonds are used for cutting glass, for which purpose only the natural curved edge of the crystal is suitable, as the cut or broken diamond merely scratches the glass superficially. The rock-boring apparatus employed in tunnelling and well-sinking is frequently fitted with diamonds set in the edge of a steel ring. Diamond-dust is the best grinding and polishing material for hard substances. For these purposes, inferior varieties of diamond may be employed. The optical properties of the diamond have caused it to be used for microscopic objectives; but the great difficulty of grinding lenses of so refractory a material has limited this application.

COMPOUNDS OF CARBON WITH OXYGEN.

CARBONIC ANHYDRIDE.

$$CO_2.$$

Molecular weight = 44. *Molecular volume* $\square\square$. 1 *litre weighs* 22 *criths. Fuses at* —57° C. (—70.6° F.) *Boils below its fusing point.*

History.—This gas was discovered by Van Helmont in the seventeenth century. It was further studied by Black, but its true chemical nature was first demonstrated by Lavoisier.

Occurrence.—Carbonic anhydride occurs in small quantity in the atmosphere, to the extent of about 3 volumes in 10,000 volumes of air. All spring-water contains it in solution, and in the case of some springs arising in volcanic districts, the quantity of carbonic anhydride dissolved is so great as to cause the water to effervesce strongly. In such volcanic districts, the gas is often given off from fissures in the earth, and this continues for thousands of years after the cessation of active volcanic phenomena.

Preparation.—1. When carbon is burned in an excess of oxygen or air carbonic anhydride is formed:

$$C + O_2 = \underset{\text{Carbonic anhydride.}}{CO_2.}$$

Unless an excess of oxygen or air is employed, carbonic oxide is also formed.

This method is sometimes employed when carbonic anhydride is required in very large quantities for manufacturing purposes, as in the preparation of white lead. Coke is burnt in atmospheric air for such applications.

2. The method usually employed in the laboratory, for the preparation of this gas in a state approximating to purity, depends on the fact that carbonates are easily decomposed by stronger acids, and that the carbonic acid thus produced instantly breaks up into carbonic anhydride and water. Calcic carbonate in its naturally occurring varieties, as chalk or marble, is the salt usually employed for this purpose. The marble, broken into coarse fragments, is introduced into a flask fitted with a funnel and delivery tube as in the apparatus for the preparation of hydrogen (Fig. 16, p. 143), and the flask is half-filled with water. Hydrochloric acid is then poured through the funnel until the gas is evolved in a sufficiently rapid stream:

$$\underset{\text{Calcic carbonate.}}{COCao''} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2} + \underset{\text{Calcic chloride.}}{CaCl_2}.$$

Other carbonates may be substituted for calcic carbonate and other acids for hydrochloric acid in the above reaction:

$$\underset{\text{Potassic carbonate.}}{COKo_2} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2} + \underset{\text{Potassic sulphate.}}{SO_2Ko_2}.$$

$$\underset{\text{Hydric potassic carbonate.}}{COHoKo} + \underset{\text{Nitric acid.}}{NO_2Ho} = \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2} + \underset{\text{Potassic nitrate.}}{NO_2Ko}.$$

3. Sulphuric acid cannot be employed, in the foregoing way, with marble in the preparation of carbonic anhydride, as the insoluble calcic sulphate coats the marble and prevents further action. But if concentrated sulphuric acid be poured upon *chalk* and then a little water be added, the gas is evolved in a steady current, as the acid under these conditions produces a disintegration of the chalk.

4. Most carbonates, when strongly heated, evolve carbonic anhydride, as for example when chalk or marble is calcined to form quicklime:

$$\underset{\text{Calcic carbonate.}}{COCao''} = \underset{\text{Calcic oxide.}}{CaO} + \underset{\text{Carbonic anhydride.}}{CO_2}.$$

The carbonates of the alkali metals are the only exceptions to this rule.

Formation.—When any substance containing carbon is burned in air, the carbon is converted into carbonic anhydride, the hydrogen with which the carbon is generally associated forming water. In this way immense quantities of carbonic anhydride are continually discharged into the atmosphere in the combustion of coal and wood.

Active combustion is a rapid oxidation. But *combined* carbon may also undergo slow oxidation with production of carbonic anhydride. Thus the slow oxidation of the animal tissues of the living body produces the carbonic anhydride which is given off from the lungs during respira-

tion. This may be shown by breathing through lime-water, which is thus rendered turbid.

In fermentation, decay, and putrefaction, processes in which complex chemical changes take place in organic matter under the influence of minute living organisms, part of the carbon of the substance is often evolved along with a portion of its oxygen as carbonic anhydride. Thus in the fermentation of grape-sugar with yeast at a temperature of about 22°:

$$\underset{\text{Grape-sugar.}}{C_6H_{12}O_6} = \underset{\text{Ethylic alcohol.}}{2C_2H_5Ho} + \underset{\text{Carbonic anhydride.}}{2CO_2}.$$

A similar evolution of carbonic anhydride occurs during the formation of coal.

Circulation of Carbon in Nature.—All the carbon present, in every form of combination, in the bodies of plants and animals is derived ultimately from the carbonic anhydride of the air. Plants, by means of the chlorophyll, or green coloring matter of their leaves, and with the aid of sunlight, decompose this carbonic anhydride, evolving the oxygen, and retaining the carbon for the purpose of building up their tissues. Animals—the herbivora directly, the carnivora indirectly—derive their entire nourishment from plants. The carbon is thus transferred to the bodies of animals, where it serves, by its oxidation, as a source of vital heat and of energy of motion. The oxygen necessary for this oxidation is absorbed during respiration by the hæmoglobin or red coloring matter of the blood, which thus serves as a carrier of oxygen to the tissues; and the carbonic anhydride formed in the oxidation is, as already stated, expelled with the breath and thus finds its way back into the atmosphere.

A similar cycle of operations occurs with hydrogen. The plant decomposes, under the same conditions, either the aqueous vapor of the atmosphere or the water contained in its own juices, evolving the oxygen and assimilating the hydrogen. A portion of the oxygen, either from the carbonic anhydride or from the water, or from both, is at the same time retained by the plant. During the oxidation of the animal tissues the hydrogen is for the most part re-oxidized to water, and in this form is exhaled or otherwise expelled from the body.

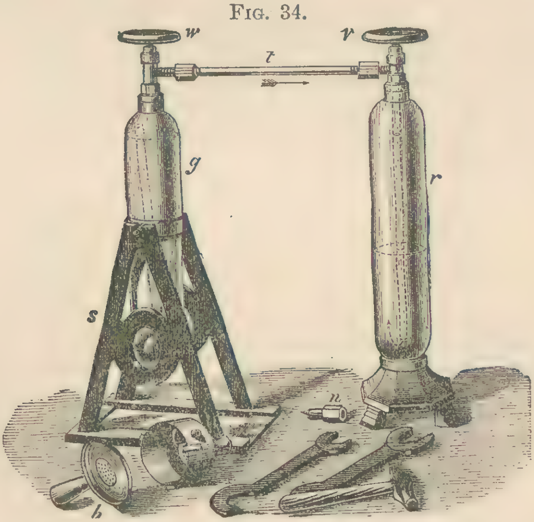
The plant thus inhales carbonic anhydride and aqueous vapor, and exhales oxygen. Animals inhale oxygen and exhale carbonic anhydride and aqueous vapor. In this way the action of the one tends to balance that of the other.

Broadly speaking, the functions of the plant may be said to be *synthetical*, those of the animal *analytical*.

Properties.—Carbonic anhydride is a colorless gas, with a slightly pungent odor and an acidulous taste. It does not support either combustion or respiration: the flame of a taper, plunged into the gas, is extinguished, and animals are rapidly asphyxiated by it. Its physiological action is that of a narcotic poison. In small quantities it may be breathed with impunity; but air containing 0.5 per cent. produces headache and oppression, and the presence of even 0.2 per cent. is sufficient to render air unwholesome.

The specific gravity of carbonic anhydride is, according to Regnault, 1.5241 (air = 1). It is thus rather more than one and a half times heavier than air. Owing to its great density it may be collected by displacement, and may be poured from one vessel into another like a liquid. On lowering a taper into the vessel into which the gas has been poured, the flame will be extinguished as soon as it is immersed in the carbonic anhydride. In like manner, if a counterpoised beaker be suspended from one arm of a balance (as in the experiment for demonstrating the lightness of hydrogen, with the exception that in the case of carbonic anhydride the beaker is suspended mouth upwards), then, on pouring the heavy gas from another vessel into the beaker, the arm of the balance supporting the beaker will be depressed by the weight of the gas. This property, which causes carbonic anhydride to collect at the lowest level, is sometimes the source of fatal accidents, as in cases where wells or beer-vats containing this gas have been incautiously entered. The phenomena of the Grotto del Cane and of the Poison Valley in Java are due to the same cause. Carbonic anhydride is formed in coal-mine explosions by the combustion of the *fire-damp*

FIG. 34.



(methylic hydride, CH_4), and it frequently happens that miners who escape the violence of the explosion are asphyxiated by the *after-damp.* It has been shown, however, that the after-damp generally also contains the much more deadly carbonic oxide.

When carbonic anhydride is subjected to a pressure of 36 atmospheres at a temperature of 0° C., it condenses to a colorless liquid. The liquefaction of the gas may be conveniently effected by means of the apparatus shown in Fig. 34, devised by Thilorier. Into the strong wrought-iron generator *g*, hydric sodic carbonate, stirred up with a little over twice its weight of water, is introduced. Sulphuric acid is poured into the inner tube (represented by dotted lines in the figure)

and the head of the generator is screwed on. The generator, which swings upon trunnions on the stand *s*, is then turned over so as to allow the sulphuric acid to flow out of the tube and mix with the hydric sodic carbonate. Carbonic anhydride is liberated according to the equation—

$2COHoNao$	+	SO_2Ho_2	=	$2CO_2$	+	SO_2Nao_2	+	$2OH_2$.
Hydric sodic carbonate.		Sulphuric acid.		Carbonic anhydride.		Sodic sulphate.		Water.

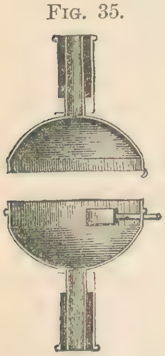
On bringing the apparatus back into its former position, the carbonic anhydride, liquefied by pressure, rises to the surface and floats as a layer on the solution of sodic sulphate. The generator is then connected by the copper tube *t* with the wrought-iron receiver *r*. On opening the screw-taps *w* and *v*, applying a gentle warmth to the generator, and cooling the receiver, the liquefied anhydride distils over into the latter vessel. The screw-tap *v* is then closed ; the generator is disconnected, emptied, recharged, and the above operations repeated. Six or seven charges suffice to fill the receiver. The nozzle *n* is then attached to the receiver in place of the tube *t*. An improved form of Thilorier's apparatus has been constructed, in which the liquefied anhydride, instead of being distilled, is forced over in the liquid state into the receiver by means of water pumped in at the base of the generator.

Liquid carbonic anhydride is colorless and very mobile. Under the influence of heat it expands more rapidly than any known substance, surpassing even the gases in this respect. The following table shows this rapid alteration of density :

Temperature.	Sp. gr.
—10° C. (14° F.)	.9951
+ 0° C. (32° F.)	.9470
+20° C. (68° F.)	.8266

Carbonic anhydride at —78° exerts a pressure of 760 mm. When the liquid is exposed to the air the heat rendered latent by its evaporation causes it to solidify. The following apparatus (Fig. 35) is well adapted for procuring solid carbonic anhydride. It consists of a circular brass box in two halves, one of which fits over the other as a lid, each half being furnished with a hollow handle covered with wood or some other bad conductor of heat. Through a small tubular opening in the circumference the nozzle of the screw-tap of the wrought-iron cylinder containing the liquefied carbonic anhydride is inserted. On opening the screw-tap a jet of liquid carbonic anhydride is projected with great violence into the brass box, and striking at a tangent to its internal circumference, flows round it, solidifying in the process, and filling the interior with a snow-like mass. On opening the box, the snowball of solid carbonic anhydride may be removed.

Fig. 35.



Solid carbonic anhydride thus prepared is a coherent white powder,

resembling snow in appearance. It may be exposed for a short time to the air; but eventually disappears as gas, without previously melting. Though its temperature is so low, it may be touched without inconvenience, as the gas which it evolves forms a non-conducting layer around it; but if it be pressed upon the skin, it produces a blister like that caused by a burn. It is soluble in ether, and in this condition its evaporation can be conveniently employed as a source of cold. When the solution of carbonic anhydride in ether is evaporated *in vacuo*, the temperature sinks so low as —110° C. (—166° F.). By means of the depression of temperature thus produced, liquid carbonic anhydride contained in a tube may be frozen into a transparent ice-like solid.

Water at 15° C. (59° F.) dissolves its own volume of carbonic anhydride under a pressure of 760 mm. The quantity of gas absorbed is approximately proportional to the pressure. (See Introduction, p. 124.) If water be saturated with the gas at a higher pressure, and the pressure be suddenly removed, evolution of gas ensues. The solubility of carbonic anhydride decreases rapidly at higher temperatures, and the whole of the dissolved gas may be expelled by boiling.

Composition.—1. When carbon is burned in oxygen, it is found that the volume of the carbonic anhydride formed is exactly equal to that of the oxygen employed. It is thus evident that carbonic anhydride contains its own volume of oxygen. In this way the composition by weight of carbonic anhydride may be deduced. Suppose the volume of oxygen employed to have been 1 litre—

1 litre of CO_2 formed weighs	22 criths.
Deduct the weight of 1 litre of O	16 "
There remain: carbon, ...	6 "

Therefore 6 parts by weight of carbon combine with 16 of oxygen to form 22 parts of carbonic anhydride. Expressed in atomic weights, this gives—

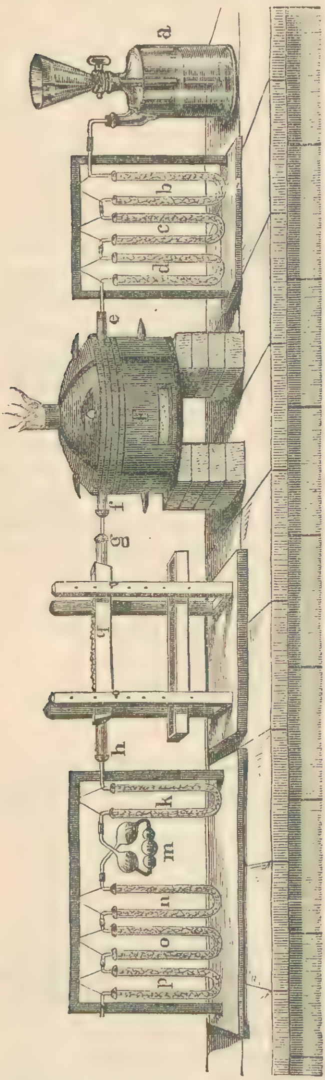
Proportion of carbon is to oxygen as 12 : 32,

corresponding to the formula CO_2.

2. The composition by weight of carbonic anhydride can be directly determined by ascertaining the weight of this gas which is formed when a known weight of pure carbon (diamond or purified graphite) is burnt in a current of oxygen. This was the method employed by Dumas and Stas. The oxygen is contained in the Woulff's bottle *a* (Fig. 36), from which it is expelled during the operation by dilute caustic potash, this liquid being employed in order to prevent the gas from being contaminated by the carbonic anhydride contained in ordinary water. It then passes through three U-tubes *b*, *c*, and *d*, the first containing pumice moistened with strong potash, the second fragments of solid potash, and the third pumice moistened with concentrated sulphuric acid. The oxygen, thus thoroughly freed from carbonic anhydride and moisture, passes on through the glazed porcelain tube *ef*, which contains the weighed portion of carbon placed in a platinum boat. This tube is

heated to redness in the furnace F, and the carbon in the boat thus burns in the current of purified oxgen. As carbonic oxide may be formed in this combustion, the gases are passed through a second tube *gh* of refractory glass, containing granulated cupric oxide, and heated to redness by means of charcoal placed in the iron trough *q*. In this way any carbonic oxide is converted into carbonic anhydride at the expense of the oxygen of the cupric oxide. The mixture of carbonic anhydride and oxygen passes on through the U-tube *k*, containing pumice and sulphuric acid; then through the Liebig's bulbs *m*, containing a strong solution of potash, by which the greater part of the carbonic anhydride is absorbed; then through the tube *n* filled with pumice moistened with strong potash, in order to absorb the last traces of carbonic anhydride. The tube *o*, containing fragments of solid potash, serves to arrest any moisture which may be given off from the tube *n*. The last tube, *p*, also containing fragments of solid patash, is introduced in order to prevent access of carbonic anhydride and moisture from the air to the tube *o*. The tubes *k*, *m*, *n*, and *o* are accurately weighed both before and after the combustion of the carbon. If the experiment has been properly conducted so as to exclude every trace of moisture, and if the carbon employed has been perfectly free from hydrogen, the tube *k* ought to show no increase in weight. The increase in weight of the tubes *m*, *n*, and *o* gives the weight of carbonic anhydride formed. The weight of carbonic anhydride, *minus* the weight of carbon employed, gives the weight of oxygen consumed. In this way it has been found that 1 gram of carbon yields 3.666 grams of carbonic anhydride. The weight of oxygen consumed is therefore 2.666 grams, from which it follows that 32 parts by weight of oxygen combine with 12 of carbon to form 44 of carbonic anhydride, a result which exactly coincides with that obtained by the foregoing method. The platinum boat ought to be weighed both before and after the experiment in order to determine the weight of ash, which is present in

FIG. 36.



even the purest forms of carbon. This weight is then deducted from the weight of carbon originally taken.

Reactions.—1. Carbonic anhydride is decomposed by the action of intense heat, such as that of the electric spark, into carbonic oxide and oxygen:

$$\underset{\text{Carbonic anhydride.}}{CO_2} = \underset{\text{Carbonic oxide.}}{CO} + O.$$

Only a small portion of the carbonic anhydride is thus decomposed, inasmuch as, when the proportion of the products of decomposition passes a certain limit, they again combine with formation of carbonic anhydride (see Introduction, p. 104).

2. When potassium is heated in an atmosphere of carbonic anhydride, the gas is decomposed with liberation of carbon:

$$\underset{\text{Carbonic anhydride.}}{3CO_2} + 2K_2 = \underset{\text{Potassic carbonate.}}{2COKo_2} + C.$$

3. Carbonic anhydride acts upon metallic hydrates, forming carbonates:

$$\underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic carbonate.}}{COKo_2} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Potassic hydrate.}}{KHo} = \underset{\text{Hydric potassic carbonate.}}{COKoHo}.$$

$$\underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Calcic hydrate.}}{CaHo_2} = \underset{\text{Calcic carbonate.}}{COCao''} + \underset{\text{Water.}}{OH_2}.$$

The carbonates are very stable compounds. The alkaline carbonates may be exposed to a white heat without undergoing decomposition; all other carbonates are decomposed at higher temperatures into metallic oxide and carbonic anhydride:

$$\underset{\text{Calcic carbonate.}}{COCao''} = \underset{\text{Calcic oxide.}}{CaO} + \underset{\text{Carbonic anhydride.}}{CO_2}.$$

The alkaline carbonates are soluble in water; all other carbonates are insoluble.

Free carbonic acid, $COHo_2$, is not known in a state of purity, but the solution of carbonic anhydride in water contains this acid. This is shown by the fact that the solution reddens litmus, a property not possessed by carbonic anhydride. Moreover, a solution of carbonic anhydride saturated under pressure loses its gas much more rapidly when freshly prepared than when the saturated solution has been preserved under pressure for some time, as in the case of artificial aërated waters.

This seems to denote that at first mere solution takes place, but that in course of time the carbonic anhydride combines chemically with the water:

$$\underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2} = \underset{\text{Carbonic acid.}}{COHo_2}.$$

With *inorganic* bases carbonic acid almost always acts as a dibasic acid, forming acid and normal salts. The acid carbonates of the alkalies are the only acid carbonates known in the solid state. *Ethereal* salts of the tetrabasic acid, CHo_4, have been prepared (see Organic Chemistry). *Dicupric carbonate*, $CCuo''_2$, which occurs as the mineral *mysorine*, may be regarded as a salt of the tetrabasic acid.

Owing to the insolubility of the carbonates of the alkaline earths, lime water or baryta water is rendered turbid by carbonic anhydride, or by a solution of a carbonate. An excess of carbonic anhydride dissolves the precipitate, owing to the formation of an acid carbonate, which, however, can exist only in solution.

CARBONIC OXIDE.

CO.

Molecular weight = 28. *Molecular volume* $\square\square$. 1 *litre weighs* 14 *criths. Liquefiable by great pressure and cold.*

History.—Carbonic oxide was discovered by Lasonne in 1776.

Preparation.—1. When carbonic anhydride is passed over red-hot charcoal, it gives up half of its oxygen to the charcoal, and carbonic oxide is formed:

$$\underset{\text{Carbonic anhydride.}}{CO_2} + C = \underset{\text{Carbonic oxide.}}{2CO}.$$

2. In like manner red-hot iron reduces carbonic anhydride to the lower stage of oxidation:

$$\underset{\text{Carbonic anhydride.}}{4CO_2} + 3Fe = \underset{\text{Triferric tetroxide.}}{{}^{iv}(Fe_3)^{viii}O_4} + \underset{\text{Carbonic oxide.}}{4CO}.$$

The reaction may be carried out by passing carbonic anhydride over iron turnings contained in a tube of porcelain or iron heated to redness in a furnace.

3. Instead of acting on free carbonic anhydride, this gas may be employed in the nascent state. Thus, if any of the carbonates which evolve carbonic anhydride at higher temperatures be heated to redness with charcoal or iron filings, carbonic oxide will be produced:

$$\underset{\text{Calcic carbonate.}}{COCao''} + C = \underset{\text{Lime.}}{CaO} + \underset{\text{Carbonic oxide.}}{2CO}.$$

4. Carbonic oxide is also formed when ferric or zincic oxide is heated to redness with charcoal:

$$\underset{\text{Zincic oxide.}}{ZnO} + C = Zn + \underset{\text{Carbonic oxide.}}{CO.}$$

5. Concentrated sulphuric acid, from its strong affinity for water, has the power of abstracting the elements of water from a number of organic substances. Thus, when oxalic acid is heated with concentrated sulphuric acid, water is removed, and a mixture of equal volumes of carbonic anhydride and carbonic oxide is evolved:

$$\underset{\text{Oxalic acid.}}{\left\{\begin{matrix} COHo \\ COHo \end{matrix}\right.} = \underset{\text{Water.}}{OH_2} + \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Carbonic oxide.}}{CO.}$$

The carbonic anhydride may be absorbed by passing the mixed gases through a strong solution of sodic hydrate. The carbonic oxide is thus obtained in a state of purity.

6. In like manner, when formic acid or a formate is heated with concentrated sulphuric acid, pure carbonic oxide is evolved:

$$\underset{\text{Formic acid.}}{\left\{\begin{matrix} H \\ COHo \end{matrix}\right.} = \underset{\text{Water.}}{OH_2} + \underset{\text{Carbonic oxide.}}{CO.}$$

7. The most convenient method of obtaining carbonic oxide for laboratory purposes consists in heating potassic ferrocyanide with from eight to ten times its weight of concentrated sulphuric acid (Fownes). The flask containing the mixture must be gently heated in order to start the reaction, which afterwards continues of itself. The evolution of gas is apt to be somewhat violent. The reaction takes place according to the following equation:

$$\underset{\text{Potassic ferrocyanide.}}{Fe''C_6N_6K_4} + \underset{\text{Water.}}{6OH_2} + \underset{\text{Sulphuric acid.}}{6SO_2Ho_2} = \underset{\text{Carbonic oxide.}}{6CO}$$

$$+ \underset{\text{Potassic sulphate.}}{2SO_2Ko_2} + \underset{\text{Ferrous sulphate.}}{SO_2Feo''} + \underset{\text{Ammonic sulphate.}}{3SO_2(NH_4O)_2.}$$

The water necessary for the reaction is derived partly from the water of crystallization of the potassic ferrocyanide, which is an aquate of the formula $Fe''C_6N_6K_4,3OH_2$, and partly from the commercial sulphuric acid, which never possesses the concentration corresponding to the pure dibasic acid SO_2Ho_2.

Formation.—When air enters a coal fire at the lower part of a grate or stove, the carbon combines with the oxygen of the air, forming car-

bonic anhydride. The carbonic anhydride passes upwards through the glowing carbon, and is in this way (see *Reaction* 1, p. 208) reduced to carbonic oxide, which may frequently be seen burning with a peculiar bluish flame where it escapes into the air at the upper part of the fire. Sometimes this carbonic oxide passes off unburnt, involving great waste of fuel. The same formation of carbonic oxide occurs on a large scale in blast furnaces.

Carbonic oxide is also formed in the destructive distillation of many organic substances containing oxygen. For this reason, it is a never-failing constituent of coal-gas.

Properties.—Carbonic oxide is a colorless gas, devoid of taste, but possessing a faint odor. It is only very slightly soluble in water. Neither the gas nor its aqueous solution has any action on litmus. It is readily inflammable, and burns in air or oxygen with a pale blue flame, forming carbonic anhydride:

$$\underset{\text{Carbonic oxide.}}{CO} + O = \underset{\text{Carbonic anhydride.}}{CO_2}.$$

Mixed with half its volume of oxygen, as expressed in the above equation, it explodes on the approach of a burning body.

It is perfectly stable at all known temperatures.

In its physiological action it displays the characteristics of a violent narcotic poison. Traces of it, if present in air, are sufficient to cause giddiness and headache when inhaled; in larger doses it produces insensibility, and even death. Small animals die quickly in an atmosphere containing 1 per cent. of this gas. Its action seems to depend on the formation of a compound of carbonic oxide with the hæmoglobin of the blood, by which the latter is prevented from exercising its function as an absorbent of oxygen. Carbonic-oxide-hæmoglobin possesses a characteristic absorption spectrum, by means of which the presence of carbonic oxide in the blood, in cases of poisoning by this gas, may be recognized. Owing to the readiness with which carbonic oxide is formed, such cases of poisoning, both accidental and intentional, occur not infrequently when the products of combustion from stoves or braziers are allowed to escape into dwelling-rooms.

Reactions.—The following reactions of carbonic oxide all depend upon its peculiar character as a compound containing dyad carbon. The carbon passes readily into its normal tetradic condition, and in this way carbonic oxide is enabled to form additive compounds.

1. At high temperatures carbonic oxide acts as a reducing agent, taking up oxygen and forming carbonic anhydride. Many of the oxides of the metals are reduced to the metallic state when heated in the gas, which in this way plays an important part in many metallurgical operations.

2. At a temperature of 80° C. (176° F.) carbonic oxide is readily absorbed by potassium, forming a compound of the formula $\left\{\begin{matrix} COK \\ COK \end{matrix}\right.$.

3. Carbonic oxide and chlorine in equal volumes unite under the influence of sunlight to form *carbonic oxydichloride* or *phosgene gas:*

$$\underset{\text{Carbonic oxide.}}{CO} + Cl_2 = \underset{\text{Carbonic oxydichloride.}}{COCl_2}.$$

Carbonic oxydichloride has a suffocating odor. At lower temperatures it condenses to a colorless liquid, boiling at 8.2° C.

4. Carbonic oxide is readily absorbed by a solution of cuprous chloride in hydrochloric acid, or by solutions of cuprous salts in ammonia. The compound with cuprous chloride crystallizes in fatty scales possessing the formula $CO(CuCl)_2,2OH_2$.

Composition.—The composition of carbonic oxide is most readily ascertained by exploding the gas with oxygen in a eudiometer. 100 c.c. of carbonic oxide and 100 c.c. of oxygen are introduced into the eudiometer, making a total of 200 c.c.

After the passage of the electric spark, it is found that the volume has been reduced to 150 c.c. Of these, 100 c.c. are absorbed by caustic potash, proving them to be carbonic anhydride. The remaining 50 c.c. are found to consist of pure oxygen. Therefore the carbonic oxide has yielded its own volume of carbonic anhydride, taking up half its volume of oxygen in the process. But it has already been proved (p. 205) that carbonic anhydride contains its own volume of oxygen; carbonic oxide therefore contains half its volume of oxygen. Expressing the volumes in litres:

1 litre of carbonic oxide weighs	14 criths.
$\frac{1}{2}$ litre of oxygen weighs	8 "
	— "
Difference, ...	6 "

The difference is the weight of carbon. In carbonic oxide the proportion of carbon to oxygen is, therefore, as 6 : 8, or, in atomic weights, as 12 : 16, and the formula of this compound is therefore **CO**.

The compounds of carbon with chlorine, nitrogen, and hydrogen, will be described under Organic Chemistry.

CHAPTER XXVI.

PENTAD ELEMENTS.

SECTION I.

NITROGEN, *Azote*, N_2.

Atomic weight = 14. *Molecular weight* = 28. *Molecular volume* ☐☐. 1 *litre weighs* 14 *criths. Liquefiable by great pressure and cold. Atomicity* ^{v}, *which, by the mutual saturation of pairs of bonds, becomes reduced to* $'''$ *or to* $'$ (see p. 80). *Evidence of atomicity:*

Nitrous oxide, ...	ON_2
Ammonia, ...	$N'''H_3$.
Ammonic chloride, ...	$N^{v}H_4Cl$.
Phosphoric fluoride (analogy), . .	$P^{v}F_5$.

History.—Nitrogen was discovered by Rutherford in 1772. He found that when an animal was allowed to breathe the air confined

under a bell-jar, and the impure air thus obtained was treated with a caustic alkali, a gas remained behind, incapable of supporting combustion or respiration. The name *nitrogen* signifies "the nitre-producer" (from *nitrum*, nitre, and γεννάω, I bring forth), and refers to the fact that this element is a constituent of nitre.

Occurrence.—Nitrogen occurs in the free state in the atmosphere, of which it forms about four-fifths by volume. Recently its presence in the sun and in some nebulæ has been rendered probable by spectrum analysis. In combination it is found in minute quantity as ammonia in the atmosphere, and it is also a constituent of numerous animal and vegetable substances.

Preparation.—1. Nitrogen is most readily obtained from atmospheric air by the removal of the oxygen. For this purpose the combustion of phosphorus is usually employed. The phosphorus is placed in a small porcelain crucible, supported by a cork floating on water, and, after setting fire to the phosphorus, a bell-jar is placed over it. The phosphorus burns, combining with the oxygen, and forming dense white clouds of phosphoric anhydride, which are speedily absorbed by the water. The nitrogen thus obtained is never quite pure, inasmuch as the phosphorus ceases to burn before the last traces of oxygen have been removed. It may be purified by leaving it in contact with moist phosphorus, which by its slow oxidation completely removes the remaining oxygen. Moist alkaline sulphides, moist ferrous sulphide, and a number of other easily oxidizable substances, act in a similar manner in removing oxygen from gaseous mixtures.

2. Very pure nitrogen may be obtained by passing a current of air, freed from carbonic anhydride and moisture, over metallic copper contained in a tube of hard glass, and heated to redness in a furnace. The oxygen of the air combines with the copper, forming cupric oxide, whilst the nitrogen passes on unchanged and may be collected.

3. On heating a concentrated solution of ammonic nitrite or a mixture of ammonic chloride and potassic or sodic nitrite, nitrogen is evolved:

$$\underset{\text{Ammonic nitrite.}}{\mathbf{N}'''\mathrm{O}(\mathrm{N^vH_4O})} = \mathrm{N_2} + \underset{\text{Water.}}{\mathbf{2OH_2}}.$$

$$\underset{\substack{\text{Ammonic}\\\text{chloride.}}}{\mathbf{NH_4}\mathrm{Cl}} + \underset{\substack{\text{Sodic}\\\text{nitrite.}}}{\mathbf{NONao}} = \underset{\substack{\text{Sodic}\\\text{chloride.}}}{\mathrm{NaCl}} + \mathrm{N_2} + \underset{\text{Water.}}{\mathbf{2OH_2}}.$$

4. Nitrogen is given off when ammonic dichromate, or a mixture of potassic dichromate with ammonic dichloride, is heated:

$$\underset{\text{Ammonic chromate.}}{\left\{\begin{matrix}\mathbf{CrO_2}(\mathrm{N^vH_4O})\\ \mathrm{O}\\ \mathbf{CrO_2}(\mathrm{N^vH_4O})\end{matrix}\right.} = \mathrm{N_2} + \underset{\text{Chromic oxide.}}{\mathbf{Cr_2O_3}} + \underset{\text{Water.}}{\mathbf{4OH_2}}.$$

5. When chlorine is passed through an excess of an aqueous solution of ammonia, the chlorine combines with the hydrogen of the ammonia, forming hydrochloric acid, which unites with the excess of ammonia, and nitrogen is liberated:

$$\underset{\text{Ammonia}}{8\mathbf{N}H_3} + 3Cl_2 = \underset{\text{Ammonic chloride.}}{6\mathbf{N}H_4Cl} + N_2.$$

The entrance of each bubble of chlorine into the solution is attended with a flash of light. Great care must be taken that the ammonia is always in excess, otherwise the very dangerously explosive compound, nitrous chloride, will be formed.

Properties.—Nitrogen is a colorless, tasteless, and inodorous gas, slightly lighter than air. It is not capable of supporting either combustion or respiration. A lighted taper is extinguished, and small animals die when plunged into this gas. It is not, however, poisonous, as is evident from the fact that it is contained in such large quantities in atmospheric air. Water dissolves only 0.025 of its bulk of the gas. Nitrogen is neither acid nor alkaline. It is one of the most indifferent bodies known, combining directly with only very few of the elements.

COMPOUNDS OF NITROGEN WITH OXYGEN AND HYDROXYL.

Nitrous oxide (*hyponitrous anhydride*),	$\mathbf{O}N_2$	$N—O—N$
or,	$''\mathbf{N}'_2O$	$\begin{array}{l} N\diagdown \\ \Vert\;\; \rangle O \\ N\diagup \end{array}$
Nitric oxide, ...	$'\mathbf{N}''O$	$—N{=}O$
Nitrous anhydride, ...	$\left\{\begin{array}{l}\mathbf{N}O \\ O \\ \mathbf{N}O\end{array}\right.$	$\begin{array}{ccc} O & & O \\ \Vert & & \Vert \\ N & —O— & N \end{array}$
Nitric peroxide, ...	$\left\{\begin{array}{l}\mathbf{N}O_2 \\ \mathbf{N}O_2\end{array}\right.$	$\begin{array}{c} O{=}N{=}O \\ \vert \\ O{=}N{=}O \end{array}$
and,	$\mathbf{N}O_2$	$\begin{array}{c} O{=}N{=}O \\ \vert \end{array}$
Nitric anhydride, ...	$\left\{\begin{array}{l}\mathbf{N}O_2 \\ O \\ \mathbf{N}O_2\end{array}\right.$	$\begin{array}{ccc} O & & O \\ \Vert & & \Vert \\ N & —O— & N \\ \Vert & & \Vert \\ O & & O \end{array}$
Hyponitrous acid, ...	$''\left\{\begin{array}{l}\mathbf{N}Ho \\ \mathbf{N}Ho\end{array}\right.$	$\begin{array}{l} N—O—H \\ \Vert \\ N—O—H \end{array}$
Nitrous acid, ...	$\mathbf{N}OHo$	$O{=}N—O—H$
Nitric acid, ...	$\mathbf{N}O_2Ho$	$\begin{array}{l} O \\ \Vert \\ N—O—H \\ \Vert \\ O \end{array}$

The most important member of the above group, and the starting-point for the preparation of all the others, is nitric acid. This compound will be described first.

NITRIC ACID, *Aquafortis*.

NO_2Ho.

Molecular weight = 63. *Fuses at* —50° C. (—58° F.). *Boils at* 86° C. (186.8° F.).

History.—Nitric acid was known to the alchemists. Lavoisier showed that it contained oxygen, but its exact composition was first ascertained by Cavendish.

Production.—1. When a series of electric sparks is passed between platinum points in a glass globe containing air, red fumes of nitric peroxide (*q.v.*) are formed. On shaking the contents of the globe with water, the red fumes disappear, and the water acquires an acid reaction, arising from the presence of nitric acid in solution. It was in this way that the formation of nitric acid was studied by Cavendish. The production of red fumes is enormously increased by passing the sparks through compressed air.

In like manner, nitric acid is formed when hydrogen is burned in oxygen containing a small proportion of nitrogen, or when an excess of the gases obtained by the electrolytic decomposition of water is mixed with air and exploded in a eudiometer. Nitric acid is also produced in the combustion of ammonia in oxygen.

2. When nitrogenous animal matter is slowly oxidized by the action of the air, at a temperature between 20° and 30° C. (68°–86° F.), in presence of water and powerful bases, nitric acid is formed, and combines with the bases to form nitrates. In this way the nitrites and nitrates which are found in the shallow well waters of towns have been formed from the nitrogenous matter contained in the soil. In hot climates, particularly in districts where there is little rain, the nitrates make their appearance as an efflorescence on the surface of the soil, as in India and in Chili.

This natural formation of potassic nitrate is imitated artificially in the so-called *nitre plantations*. In these, animal matters mixed with lime and ashes, are placed in loose heaps, exposed to the air but sheltered from rain. From time to time the heaps are watered with urine and stable runnings. The nitre bed is usually lixiviated every three years, and the product, consisting chiefly of calcic nitrate, is converted by treatment with potassic carbonate into potassic nitrate, which is purified by crystallization. In this way a cubic metre of earth may, under favorable conditions, be made to yield as much as 20 kilos. of nitre.

Nitrification appears to depend upon the presence of an organized ferment.

Manufacture.—Nitric acid is prepared by distilling potassic nitrate

(nitre) or sodic nitrate (cubic nitre or Chili saltpetre) with concentrated sulphuric acid:

$\mathbf{NO_2}Ko$	$+$	$\mathbf{SO_2}Ho_2$	$=$	$\mathbf{SO_2}HoKo$	$+$	$\mathbf{NO_2}Ho$
Potassic nitrate.		Sulphuric acid.		Hydric potassic sulphate.		Nitric acid.

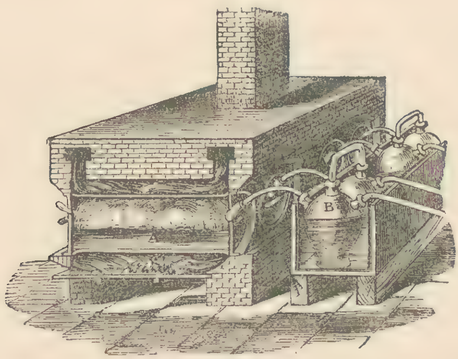
By employing two molecules of potassic nitrate to one of sulphuric acid, a saving of sulphuric acid is effected, but a higher temperature is required, which destroys some of the nitric acid. In this case the reaction takes place in two stages, of which the first is expressed in the above equation, whilst in the second, the hydric potassic sulphate acts upon another molecule of potassic nitrate:

$\mathbf{SO_2}HoKo$	$+$	$\mathbf{NO_2}Ko$	$=$	$\mathbf{SO_2}Ko_2$	$+$	$\mathbf{NO_2}Ho$
Hydric potassic sulphate.		Potassic nitrate.		Potassic sulphate.		Nitric acid.

A further disadvantage of the second method lies in the fact that the normal potassic sulphate can be removed from the retort only in the solid state, whereas the hydric potassic sulphate, from its greater fusibility, can be poured out.

On a commercial scale the distillation is performed in cast-iron cylinders A (Fig. 37) lined with fire-clay and heated over a furnace. The distillate is condensed in large stoneware Woulff's bottles, B, each con-

Fig. 37.



nected with the one following. The last of these leads into a coke tower, down which a stream of water trickles. Any fumes of nitric peroxide which have escaped condensation in the Woulff's bottles are absorbed by the water in the coke tower.

Chili saltpetre is generally employed in the manufacture of nitric acid. It is cheaper than nitre, and, owing to the lower atomic weight of sodium, yields a larger proportion of nitric acid.

The acid thus obtained may be purified by distillation with its own volume of concentrated sulphuric acid. The distillate contains from 99.5 to 99.8 per cent. of $\mathbf{NO_2}Ho$.

Properties.—Pure nitric acid is a colorless fuming liquid of sp. gr. 1.53. It has an irritating odor, and is powerfully corrosive, cauterizing the skin and staining it yellow. It begins to boil at 86° C. (187° F.), but is partially decomposed into nitric peroxide, oxygen, and water, so that gradually the distillate becomes weaker, and the boiling point rises, till at last an acid containing 68 per cent. of $\mathbf{N}O_2Ho$, and boiling at 120.5° C. (248.9° F.), distils over under ordinary pressure without further change. This acid has a sp. gr. of 1.414 at 15° C. (59° F.), and is the ordinary concentrated nitric acid of commerce. If a weaker acid be distilled, the liquid in the retort becomes gradually more concentrated, till the acid containing 68 per cent. is obtained, which then distils unchanged. Notwithstanding the constancy of its boiling point, this acid is not a definite compound. By varying the pressure under which the distillation is performed, acids of varying strength may be obtained, but for each of these pressures, there is a fixed strength of acid with a constant boiling point. Under a pressure of 70 mm. an acid containing only 66.7 per cent. of $\mathbf{N}O_2Ho$ distils over between 65° and 70° C. (149°–158° F.). The higher pressure thus corresponds to the greater strength of acid, the reverse being the case with hydrochloric acid (see p. 158).

When concentrated nitric acid is mixed with water, diminution of volume and elevation of temperature ensue. The following table contains the specific gravities of various strengths of aqueous acid at 0° and 15° C. (32°–59° F.), as determined by J. Kolb:

Per cent. $\mathbf{N}O_2Ho$.	Sp. gr. at 0° C. (32° F.).	Sp. gr. at 15° C. (59° F.).
100.00	1.559	1.530
90.0	1.522	1.495
80.0	1.484	1.460
70.0	1.444	1.423
60.0	1.393	1.374
50.0	1.334	1.317
40.0	1.267	1.251
30.0	1.200	1.185
20.0	1.132	1.120
15.0	1.099	1.089
10.0	1.070	1.060
5.0	1.031	1.029

The decomposition which concentrated nitric acid undergoes under the influence of heat is expressed by the following equation:

$$\underset{\text{Nitric acid.}}{4\mathbf{N}O_2Ho} = \underset{\text{Water.}}{2OH_2} + \underset{\text{Nitric peroxide.}}{2'\mathbf{N}^{iv}_2O_4} + O_2.$$

This decomposition is very rapid at 100° C., and on this property the powerful oxidizing action of hot nitric acid depends.

Concentrated nitric acid, when exposed to the action of light, turns yellow, owing to a decomposition similar to the above.

Reactions.—1. With metallic oxides or hydrates nitric acid yields nitrates:

$$\underset{\text{Potassic hydrate.}}{OKH} + \underset{\text{Nitric acid.}}{NO_2Ho} = \underset{\text{Potassic nitrate.}}{NO_2Ko} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\text{Plumbic oxide.}}{PbO} + \underset{\text{Nitric acid.}}{2NO_2Ho} = \underset{\text{Plumbic nitrate.}}{\begin{matrix}NO_2\\NO_2\end{matrix}Pbo''} + \underset{\text{Water.}}{OH_2}.$$

2. The action of nitric acid upon metals is of a somewhat complicated character, varying not only with different metals, but also, for the same metal, with the strength of the acid employed and the temperature at which the reaction takes place. Nitrates of the metals are formed, but at the same time another portion of the nitric acid is reduced to some lower oxide of nitrogen. Thus, silver, copper, and mercury, are attacked by nitric acid acid with formation of nitrates and evolution of nitric oxide:

$$3Cu + \underset{\text{Nitric acid.}}{8NO_2Ho} = \underset{\text{Cupric nitrate.}}{3\left\{\begin{matrix}NO_2\\Cuo''\\NO_2\end{matrix}\right.} + \underset{\text{Nitric oxide.}}{2'N''O} + \underset{\text{Water.}}{4OH_2}.$$

With very concentrated acid, nitric peroxide ($'N^{iv}{}_2O_4$) is generally evolved, and when the reaction takes place at a high temperature, a portion of the nitric acid is completely reduced to nitrogen. When silver is slowly dissolved by weak nitric acid in the cold, nitrous acid is formed.

When nitric acid acts upon copper in presence of much cupric nitrate, the gas evolved consists chiefly of nitrous oxide.

When nitric acid acts upon a more electro-positive metal, such as zinc, nitrous oxide is evolved, and when a very concentrated acid is employed, ammonia is formed and combines with the excess of nitric acid:

$$4Zn + \underset{\text{Nitric acid.}}{10NO_2Ho} = \underset{\text{Nitrous oxide.}}{ON_2} + \underset{\text{Zincic nitrate.}}{4\left\{\begin{matrix}NO_2\\Zno''\\NO_2\end{matrix}\right.} + \underset{\text{Water.}}{5OH_2}.$$

$$4Zn + \underset{\text{Nitric acid.}}{9NO_2Ho} = \underset{\text{Zincic nitrate.}}{4\left\{\begin{matrix}NO_2\\Zno''\\NO_2\end{matrix}\right.} + \underset{\text{Water.}}{3OH_2} + \underset{\text{Ammonia.}}{NH_3}.$$

By the action of zinc in an alkaline solution, the whole of the nitric acid present is reduced to ammonia by the nascent hydrogen. The ammonia may be distilled off and absorbed in a solution of hydrochloric acid. This method is employed in the quantitative estimation of nitric acid.

3. The general action of nitric acid is that of a powerful oxidizing agent. Sulphur, phosphorus, carbon, amorphous boron and silicon,

arsenic, and iodine, are converted by treatment with nitric acid into sulphuric, phosphoric, carbonic, boric, silicic, arsenic, and iodic acids. In the case of phosphorus the oxidation takes place with explosive violence, and if the concentrated acid be dropped upon hot sawdust or finely powdered charcoal, the latter inflames.

It has been mentioned under the heading of hydrochloric acid that oxidizing agents liberate chlorine from this acid. In this way chlorine is evolved from a mixture of nitric and hydrochloric acids:

$$\underset{\text{Nitric acid.}}{NO_2Ho} + \underset{\text{Hydrochloric acid.}}{3HCl} = \underset{\substack{\text{Nitrous oxychloride.}\\\text{(Nitrosylic chloride.)}}}{NOCl} + \underset{\text{Water.}}{2OH_2} + Cl_2.$$

This mixture was known to the alchemists, who gave to it the name *aqua-regia*, from its power of dissolving gold, the *king* of metals. It is employed in the laboratory as a solvent for gold, platinum, and various ores. The solvent action depends on the presence of the chlorine evolved in the above reaction.

The action of nitric acid on organic compounds will be studied in connection with these (Organic Chemistry).

Nitrates.—Nitric acid is generally monobasic. The numerous so-called basic nitrates may, however, be regarded as salts of tribasic and pentabasic nitric acid ($NOHo_3$ and NHo_5). Graham first pointed out that in basic salts the base frequently replaces the water of crystallization of the normal salt. This supposed water of crystallization must, therefore, in as far as it may be replaced by a base, be regarded as water of constitution. Thus cupric nitrate

$\left(\begin{matrix}NO_2\\NO_2\end{matrix}Cuo'',3OH_2\right)$ and basic cupric nitrate $\left(\begin{matrix}NO_2\\NO_2\end{matrix}Cuo'',2CuO,OH_2\right)$

might be formulated $\begin{matrix}NOHo_2\\NOHo_2\end{matrix}Cuo'',OH_2$ and $\begin{matrix}NOCuo''\\NOCuo''\end{matrix}Cuo'',OH_2$.

The monobasic nitrates are all soluble in water.

At a high temperature the nitrates are all decomposed. They generally evolve, first, pure oxygen, then nitric peroxide, or a mixture of nitrogen and oxygen, whilst an oxide of the metal is left.

The presence of nitrates in solution may be recognized by the following characteristic reaction: The solution supposed to contain a nitrate is mixed in a test-tube with a solution of ferrous sulphate. Concentrated sulphuric acid is then poured down the side of the sloping tube, so as to sink to the bottom of the liquid without mixing with it. If a nitrate is present, a characteristic brown coloration will be visible at the surface of contact of the two layers. The explanation of this is that the nitric acid, liberated by the sulphuric acid, is reduced by the ferrous sulphate to nitric oxide, the latter dissolving in the excess of ferrous sulphate with a brown color.

NITRIC ANHYDRIDE.

N_2O_5.

Probable molecular weight = 108. *Fuses at* 29.5° C. *Boils at* 45° C.

History.—Nitric anhydride was discovered by Deville in 1849.

Preparation.—1. This compound is formed when dry chlorine is passed over dry argentic nitrate contained in a U-tube and heated in a water-bath. The reaction takes place in two stages. In the first of these nitric dioxychloride, a volatile liquid, is formed:

$$\underset{\text{Argentic nitrate.}}{NO_2Ago} + Cl_2 = \underset{\text{Nitric dioxychloride.}}{NO_2Cl} + \underset{\text{Argentic chloride.}}{AgCl} + O.$$

In the second the nitric dioxychloride acts on the unattacked argentic nitrate:

$$\underset{\text{Argentic nitrate.}}{NO_2Ago} + \underset{\text{Nitric dioxychloride.}}{NO_2Cl} = \underset{\text{Nitric anhydride.}}{N_2O_5} + \underset{\text{Argentic chloride.}}{AgCl.}$$

The reaction begins at 95° C. (203° F.), and, when once started, continues, even when the temperature is allowed to fall as low as 60° C. (140° F.). All unnecessary heating must be avoided, as the anhydride is totally decomposed at a temperature very slightly above that required for its formation. The anhydride distils over, and is condensed in a tube surrounded by a freezing mixture.

2. Nitric anhydride may also be obtained by abstracting the elements of water from nitric acid by means of phosphoric anhydride:

$$\underset{\text{Nitric acid.}}{2NO_2Ho} = \underset{\text{Nitric anhydride.}}{N_2O_5} + \underset{\text{Water.}}{OH_2.}$$

The phosphoric anhydride is added very gradually to the concentrated nitric acid, cooled by ice, and the pasty mass is afterwards distilled at a low temperature. The anhydride collects as a crystalline mass in the receiver.

Properties.—Nitric anhydride forms large colorless prisms, which fuse at 29.5° C. (85.1° F.) It boils with decomposition and evolution of brown fumes about 45° C. (113° F.). When sealed in a glass tube, it may be preserved unaltered, if kept in a cool place; but, in a warm room, gradually undergoes decomposition into oxygen and nitric peroxide, ultimately fracturing the tube with the internal pressure.

When thrown into water the anhydride hisses violently, evolving great heat, and combining with the water to form nitric acid:

$$\underset{\text{Nitric anhydride.}}{N_2O_5} + \underset{\text{Water.}}{OH_2} = \underset{\text{Nitric acid.}}{2NO_2Ho.}$$

NITROUS OXIDE, *Hyponitrous Anhydride, Laughing Gas.*

$$ON_2.$$

Molecular weight = 44. *Molecular volume* ☐☐. 1 *litre weighs* 22 *criths.* *Fuses at* —101° C. (—149.8° F.). *Boils at* —88° C. (—126.4° F.).

History.—This compound was discovered by Priestley in 1772.

Preparation.—1. Nitrous oxide is formed by the action of dilute nitric acid upon zinc:

$$\underset{\text{Nitric acid.}}{10NO_2Ho} + 4Zn = \underset{\text{Nitrous oxide.}}{ON_2} + \underset{\text{Zincic nitrate.}}{4\left\{\begin{matrix}NO_2\\Zno''\\NO_2\end{matrix}\right.} + \underset{\text{Water.}}{5OH_2}.$$

This method does not, however, yield the compound in a state of purity, and is never employed in its preparation.

2. Nitrous oxide may readily be obtained in large quantity by heating ammonic nitrate. Under the influence of heat, the elements of water are removed from this salt and nitrous oxide is formed:

$$\underset{\text{Ammonic nitrate.}}{NO_2(N^vH_4O)} = \underset{\text{Water.}}{2OH_2} + \underset{\text{Nitrous oxide.}}{ON_2}$$

The ammonic nitrate, previously dried, is heated in a flask to which a delivery tube is attached. The heat must not be applied too suddenly, otherwise the decomposition takes place with explosive violence, and nitric oxide is formed. The gas is purified by passing it first through a solution of ferrous sulphate, in order to absorb nitric oxide, and then through caustic potash, to free it from chlorine derived from ammonic chloride contained in the commercial nitrate. It may be collected over mercury, or over warm water, in which it is less soluble than in cold water.

Properties.—Nitrous oxide is a colorless gas with a faint pleasant odor, and a sweetish taste. Its density is 1.527 (air = 1). Water dissolves about four-fifths of its volume of the gas, and alcohol takes up a still larger quantity.

Nitrous oxide supports the combustion of bodies which burn in oxygen. A glowing match is rekindled when plunged into the gas, and burns almost as brightly as in oxygen. Phosphorus burns with a flame of dazzling brightness. Feebly burning sulphur is extinguished by the gas, but, if burning strongly, the combustion continues with great vigor.

All combustions in nitrous oxide are effected solely at the expense of the oxygen contained in the gas, the nitrogen taking no part in the reaction. In order that combustion may continue, it is necessary that the temperature of the burning body should be sufficiently high to decompose the nitrous oxide into nitrogen and oxygen. If this condition is

not fulfilled, combustion is impossible, as may be seen in the case of feebly burning sulphur. Strictly speaking, therefore, nitrous oxide, as such, does not support combustion. It does so only by the agency of one of its products of decomposition—oxygen.

Nitrous oxide was first liquefied by Faraday, by heating ammonic nitrate in a bent tube (see p. 155). It may be most conveniently liquefied with the aid of a force-pump, cooling the wrought-iron receiver with ice. Liquid nitrous oxide is colorless, and very mobile. It boils at —88° C. (—126.4° F.) under atmospheric pressure, whilst at 0° C. the tension of its vapor is 30 atmospheres. By means of the cold produced by its own evaporation, or by plunging a tube containing it into a bath of solid carbonic anhydride in ether, and allowing this freezing mixture to evaporate *in vacuo*, liquid nitrous oxide may be frozen into colorless crystals resembling in appearance ammonic nitrate. By the evaporation *in vacuo* of a mixture of liquid nitrous oxide and carbonic disulphide, a degree of cold equal to —140° C. (—220° F.) may be obtained. Liquid nitrous oxide, in spite of its low boiling point, may be preserved in open glass tubes for over half an hour. If mercury be poured into this liquid, the metal is instantly frozen.

Nitrous oxide, when inhaled, acts as a narcotic poison. In smaller doses it produces temporary nervous exhilaration or intoxication; hence the name *laughing gas*. It is employed in minor surgical operations as an anæsthetic.

Composition.—The composition of nitrous oxide may be ascertained by heating sodium in a bent glass tube containing a measured volume of the gas over mercury (see p. 159). The sodium combines with the oxygen of the gas, forming solid sodic oxide, and liberating the nitrogen. After the action is finished, the gas remaining in the tube is found to possess exactly the same volume as the gas employed, and may be shown to consist of pure nitrogen. Hence nitrous oxide contains its own volume of nitrogen. Expressing the volumes in litres—

1 litre of nitrous oxide weighs	22 criths.
Deduct weight of litre of nitrogen, . . .	14 "
There remain	8 "

which is the weight of $\frac{1}{2}$ litre of oxygen. One litre of nitrous oxide therefore contains 1 litre of nitrogen and $\frac{1}{2}$ litre of oxygen; or, 2 volumes of nitrogen combine with 1 volume of oxygen to form 2 volumes of nitrous oxide. Expressed in atomic weights, 28 parts by weight of nitrogen combine with 16 of oxygen to form 44 of nitrous oxide.

HYPONITROUS ACID.

$$''\begin{cases} \mathbf{N}Ho \\ \mathbf{N}Ho \end{cases}$$

Known only in its salts, or in aqueous solution.

Preparation of Argentic Hyponitrite ($''\mathbf{N}'_2Ago_2$).—When an aqueous solution of potassic nitrate is treated with sodium amalgam in the proportion of four atoms of sodium to one molecule of nitrate, a reduction of the nitrate takes place according to the following equation:

$$\underset{\text{Potassic nitrate.}}{2\mathbf{N}O_2Ko} + 4H_2 = \underset{\text{Potassic hyponitrite.}}{''\mathbf{N}'_2Ko_2} + \underset{\text{Water.}}{4\mathbf{O}H_2}.$$

Potassic nitrite is formed as an intermediate product in this reaction, and a saving of sodium amalgam may be effected by starting from the nitrite:

$$\underset{\text{Potassic nitrite.}}{2\mathbf{N}OKo} + 2H_2 = \underset{\text{Potassic hyponitrite.}}{''\mathbf{N}'_2Ko_2} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

The alkaline liquid obtained by either of these processes is then accurately neutralized with acetic acid, and argentic nitrate is added. Argentic hyponitrite is thus obtained as a greenish-yellow precipitate, which, by solution in dilute nitric acid and precipitation with ammonia, acquires a pure yellow color.

Properties.—Argentic hyponitrite may be dissolved in weak acids without suffering immediate decomposition, but the solution is very unstable.

A solution of potassic hyponitrite acidulated with acetic acid undergoes decomposition on heating, the liberated hyponitrous acid breaking up into nitrous oxide and water:

$$''\mathbf{N}'_2Ho_2 = ''\mathbf{N}'_2O + \mathbf{O}H_2.$$

Hence nitrous oxide may be considered as the anhydride of hyponitrous acid.

The acid salts of hyponitrous acid are known only in solution. Thus baric hyponitrite, $''\left\{\begin{matrix}\mathbf{N}\\\mathbf{N}\end{matrix}\right.Bao''$, which is insoluble in water, dissolves in aqueous hyponitrous acid with formation of an acid salt. The existence of this salt proves that hyponitrous acid must be at least dibasic.

NITROUS ANHYDRIDE.

$$\mathbf{N}_2O_3.$$

Probable molecular weight = 76.

Preparation.—1. When nitric acid is heated along with bodies capable of taking up oxygen, such as arsenious acid or starch, nitrous anhydride is formed:

$$\underset{\text{Arsenious anhydride.}}{\mathbf{As}_2O_3} + \underset{\text{Nitric acid.}}{2\mathbf{N}O_2Ho} = \underset{\text{Arsenic anhydride.}}{\mathbf{As}_2O_5} + \underset{\text{Nitrous anhydride.}}{\mathbf{N}_2O_3} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

The nitrous anhydride thus obtained is mixed with nitric peroxide.

2 Nitrous anhydride may also be prepared by mixing 4 volumes of nitric oxide with 1 volume of oxygen. Direct combination takes place according to the equation:

$$\underset{\text{Nitric oxide.}}{2'\mathbf{N}''O} + O = \underset{\text{Nitrous anhydride.}}{\mathbf{N}_2O_3}.$$

Properties.—Nitrous anhydride prepared by either of the above reactions is a reddish gas, which by passing through a U-tube immersed in a freezing mixture, may be condensed to a blue liquid. It is a very unstable compound, and undergoes gradual decomposition, even below 0° C., into nitric oxide and nitric peroxide:

$$\underset{\text{Nitrous anhydride.}}{N_2O_3} = \underset{\text{Nitric oxide.}}{'N''O} + \underset{\text{Nitric peroxide.}}{'N^{iv}O_2}$$

On warming, this decomposition is very rapid.

The addition of a small quantity of water to nitrous anhydride converts it into nitrous acid:

$$\underset{\text{Nitrous anhydride.}}{N_2O_3} + \underset{\text{Water.}}{OH_2} = \underset{\text{Nitrous acid.}}{2NOHo.}$$

A larger quantity of water decomposes the compound with effervescence: nitric oxide is evolved, and nitric acid remains in solution:

$$\underset{\text{Nitrous anhydride.}}{3N_2O_3} + \underset{\text{Water.}}{OH_2} = \underset{\text{Nitric acid.}}{2NO_2Ho} + \underset{\text{Nitric oxide.}}{4'N''O.}$$

The two foregoing reactions illustrate strikingly the inadequacy of chemical equations as expressions of chemical change. In the first equation, the proportion of water to nitrous anhydride is three times as great as in the second; yet the first stands for a reaction in which only a small quantity of water is required, and the second for a reaction which occurs only in presence of an excess of water. The reason of this discrepancy is that ordinary equations take no account of the relative masses of the reacting substances, and the mass of a substance is frequently an important factor, determining in some cases the direction of the chemical change.

NITROUS ACID.

NOHo.

Molecular weight = 47.

Preparation.—Nitrous acid may be obtained by mixing liquefied nitrous anhydride with water as above described. It cannot be prepared in a state of purity, and is an exceedingly unstable compound.

Decompositions.—1. In the presence of much water nitric acid and nitric oxide are formed:

$$\underset{\text{Nitrous acid.}}{3NOHo} = \underset{\text{Nitric acid.}}{NO_2Ho} + \underset{\text{Nitric oxide.}}{2'N''O} + \underset{\text{Water.}}{OH_2.}$$

2. Under some circumstances nitrous acid acts as a reducing agent:

$$\underset{\text{Nitrous acid.}}{2NOHo} + O_2 = \underset{\text{Nitric acid.}}{2NO_2Ho.}$$

In this way acidulated solutions of the nitrites decolorize potassic permanganate, reduce soluble chromates to green chromic salts, and precipi-

tate gold and mercury in the metallic state from solutions of their salts.

3. In many other cases nitrous acid displays oxidizing properties:

$$\underset{\text{Nitrous acid.}}{4\mathbf{NO}\text{Ho}} = \underset{\text{Nitric oxide.}}{4'\mathbf{N}''\text{O}} + \underset{\text{Water.}}{2\mathbf{O}\text{H}_2} + \text{O}_2.$$

Thus acid solutions of the nitrites liberate iodine from potassic iodide and bleach a solution of indigo.

Nitrites.—With metallic oxides or hydrates, nitrous acid forms nitrites:

$$\underset{\substack{\text{Potassic}\\\text{hydrate.}}}{\mathbf{O}\text{KH}} + \underset{\substack{\text{Nitrous}\\\text{acid.}}}{\mathbf{NO}\text{Ho}} = \underset{\substack{\text{Potassic}\\\text{nitrite.}}}{\mathbf{NO}\text{Ko}} + \underset{\text{Water.}}{\mathbf{O}\text{H}_2}.$$

The alkaline nitrites may be most readily obtained by cautiously heating the nitrates. An addition of copper or lead facilitates the reaction by aiding in the removal of the oxygen:

$$\underset{\substack{\text{Potassic}\\\text{nitrate.}}}{2\mathbf{NO}_2\text{Ko}} = \underset{\substack{\text{Potassic}\\\text{nitrite.}}}{2\mathbf{NO}\text{Ko}} + \text{O}_2.$$

The temperature must not be raised too high, otherwise the nitrite will be decomposed. The alkaline nitrites are soluble in alcohol, and may thus be separated from unaltered nitrate, which is insoluble.

The nitrites evolve reddish vapors when treated with dilute acids, and may thus be distinguished from the nitrates, which do not possess this property.

NITRIC OXIDE.

$'\mathbf{N}''\text{O}.$

Molecular weight = 30. *Molecular volume* $\square\square$. 1 *litre weighs* 15 *criths. Liquefiable by great pressure and cold.*

History.—Nitric oxide was discovered by Van Helmont, who, however, failed to recognize its true character. It was first investigated by Priestley.

Preparation.—1. Nitric oxide is formed when nitric acid acts upon mercury or copper:

$$3\text{Cu} + \underset{\text{Nitric acid.}}{8\mathbf{NO}_2\text{Ho}} = \underset{\text{Cupric nitrate.}}{3\left\{\begin{matrix}\mathbf{NO}_2\\ \text{Cuo}''\\ \mathbf{NO}_2\end{matrix}\right.} + \underset{\text{Nitric oxide.}}{2'\mathbf{N}''\text{O}} + \underset{\text{Water.}}{4\mathbf{O}\text{H}_2}.$$

The gas is purified by passing it through a solution of caustic soda.

Nitric oxide thus prepared is apt to contain nitrous oxide and free nitrogen, particularly towards the end of the reaction. In order to purify the product, advantage is taken of the property which nitric

oxide possesses of dissolving in a concentrated solution of ferrous sulphate. The solution of this salt absorbs the gas in large quantity, forming a compound of the formula $2SO_2Feo'','N''O$, which remains dissolved in the liquid, imparting to it a deep brown color. On heating this brown liquid, pure nitric oxide is evolved.

2. Nitric oxide may be readily obtained in a state of purity by acting upon nitric acid with ferrous sulphate. A convenient mode of applying this reaction consists in introducing into a retort 30 grams of nitre with 240 grams of ferrous sulphate, and pouring in through a funnel 250 cubic centimetres of a mixture of sulphuric acid with three times its bulk of water:

$$\underset{\text{Ferrous sulphate.}}{6SO_2Feo''} + \underset{\text{Potassic nitrate.}}{2NO_2Ko} + \underset{\text{Sulphuric acid.}}{5SO_2Ho_2} = \underset{\text{Nitric oxide.}}{2'N''O} + 3\underset{\text{Ferric sulphate.}}{\left\{\begin{array}{l} SO_2- \\ SO_2-('Fe'''_2O_6)^{vi} \\ SO_2- \end{array}\right.}$$

$$+ \underset{\text{Hydric potassic sulphate.}}{2SO_2HoKo} + \underset{\text{Water.}}{4OH_2}.$$

Properties.—Nitric oxide is a colorless gas of density 1.039 (air = 1). Water dissolves one-twentieth of its volume of the gas. Neither the gas nor its aqueous solution exerts any action upon litmus.

The molecular formula NO, deduced from the vapor-density of this compound, is anomalous. This formula involves the assumption that the molecule contains an odd number of unsatisfied bonds (see Note, p. 179).

Although nitric oxide contains, for the same volume of nitrogen, twice as much oxygen as nitrous oxide, it does not support combustion so readily, owing to its greater stability. Feebly ignited charcoal is extinguished when plunged into the gas, whereas strongly glowing charcoal burns in it with great brilliancy. Phosphorus may be melted in the gas without igniting, and the flame of feebly burning phosphorus is extinguished by it; but phosphorus already well ignited continues to burn in it, emitting an intense light. Sulphur, even when burning strongly, is extinguished by nitric oxide. A mixture of nitric oxide and the vapor of carbonic disulphide burns with a vivid blue flame, very rich in chemically active rays.

Reactions.—1. When nitric oxide and oxygen are mixed, a reddish gas is formed, consisting of nitrous anhydride and nitric peroxide, both of which compounds are produced by the direct union of the nitric oxide with the oxygen:

$$\underset{\text{Nitric oxide.}}{4'N''O} + O_2 = \underset{\text{Nitrous anhydride.}}{2N'''_2O_3}.$$

$$\underset{\text{Nitric oxide.}}{2'N''O} + O_2 = \underset{\text{Nitric peroxide.}}{'N^{iv}_2O_4}.$$

These gases are absorbed by water, to which they impart an acid reaction.

2. Nitric oxide also combines directly with chlorine to form nitrous oxychloride (*q.v.*):

$$2'\mathbf{N}''O + Cl_2 = 2\mathbf{N}OCl.$$

Nitric oxide. Nitrous oxychloride. (Nitrosylic chloride.)

The direct union which occurs in the above cases is probably dependent on the presence of a free bond in the nitrogen atom of nitric oxide, and the reactions consist in the saturation of this free bond by some suitable element.

Composition.—The composition of nitric oxide may be determined in the same manner as that of nitrous oxide (see p. 221), but potassium must be employed, as sodium merely melts in the gas without decomposing it. After the reaction is finished, it is found that the original volume has decreased by one-half, and that the residual gas is pure nitrogen.

1 litre of nitric oxide weighs	15	criths.
Deduct weight of $\frac{1}{2}$ litre of nitrogen, . . .	7	"
There remain	8	"

which is the weight of $\frac{1}{2}$ litre of oxygen. One litre of nitric oxide contains therefore $\frac{1}{2}$ litre of nitrogen and $\frac{1}{2}$ litre of oxygen; or 1 volume of nitrogen combines with 1 vol. of oxygen to form 2 vols. of nitric oxide. Expressed in atomic weights, 14 parts by weight of nitrogen combine with 16 of oxygen to form 30 of nitric oxide.

NITRIC PEROXIDE.

$'\mathbf{N}^{iv}O_2$ *at higher temperatures.*

$\left\{\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\right.$, or $'\mathbf{N}^{iv}{}_2O_4$, *at lower temperatures.*

Molecular weight = 46 *and* 92. *Molecular volume* ☐☐. 1 *litre weighs* 23 *to* 46 *criths. Fuses at* — 9° C. (15.8° F.). *Boils at* 22° C. (71.6° F.).

Preparation.—1. Nitric peroxide may be obtained by the union of 2 volumes of nitric oxide with 1 of oxygen (see preceding page). The red gas thus formed may be condensed in a U-tube immersed in a freezing mixture.

2. Nitric peroxide is most conveniently prepared by the action of nitric acid on arsenious anhydride:

$$\mathbf{As}_2O_3 + 4\mathbf{N}O_2Ho = \mathbf{As}_2O_5 + 2'\mathbf{N}^{iv}{}_2O_4 + 2OH_2.$$

Arsenious anhydride. Nitric acid. Arsenic anhydride. Nitric peroxide. Water.

Small fragments of arsenious anhydride are introduced into a retort with sufficient nitric acid of sp. gr. 1.393 to cover them. The reaction takes place on gently heating, and a mixture of nitric peroxide and nitrous anhydride condenses in the receiver, which is cooled by a freezing mixture. By passing a slow current of oxygen through this mixed product, the whole of the nitrous anhydride is converted into peroxide.

3. Certain nitrates, when subjected to destructive distillation, are decomposed into nitric peroxide, oxygen, and an oxide of the metal. Plumbic nitrate is well suited for this purpose:

$$\underset{\text{Plumbic nitrate.}}{\left\{\begin{matrix}\mathbf{NO_2}\\ \mathrm{Pbo''}\\ \mathbf{NO_2}\end{matrix}\right.} = + \underset{\text{Plumbic oxide.}}{\mathbf{Pb}\mathrm{O}} + \underset{\text{Nitric peroxide.}}{{}'\mathbf{N}^{iv}{}_2\mathrm{O}_4} + \mathrm{O}.$$

The thoroughly dried plumbic nitrate is heated in a retort connected with a U-tube which is drawn out at its further extremity to a fine opening and surrounded by a freezing mixture. The liquefied nitric peroxide collects in the tube, whilst the oxygen escapes through the fine opening.

4. It is also formed by the action of nitric acid on tin:

$$\mathrm{Sn}_5 + \underset{\text{Nitric acid.}}{20\mathbf{NO}_2\mathrm{Ho}} = \underset{\text{Metastannic acid.}}{\mathbf{Sn}_5\mathrm{O}_5\mathrm{Ho}_{10}} + \underset{\text{Water.}}{5\mathbf{O}\mathrm{H}_2} + \underset{\text{Nitric peroxide.}}{10'\mathbf{N}^{iv}{}_2\mathrm{O}_4}.$$

5. Nitric peroxide is also formed by the action of nitric dioxychloride on argentic nitrite:

$$\underset{\text{Argentic nitrite.}}{\mathbf{NO}\mathrm{Ago}} + \underset{\substack{\text{Nitric dioxychloride.}\\ \text{(Nitroxylic chloride.)}}}{\mathbf{NO}_2\mathrm{Cl}} = \underset{\text{Nitric peroxide.}}{\left\{\begin{matrix}\mathbf{NO_2}\\ \mathbf{NO_2}\end{matrix}\right.} + \underset{\text{Argentic chloride.}}{\mathrm{AgCl}}.$$

Properties.—Nitric peroxide is a volatile liquid which solidifies at —9° C. (15.8° F.), forming a white fibrous crystalline mass. Nitric peroxide displays remarkable changes of color, dependent upon the temperature. Just above its fusing point it is a colorless liquid. At 0° C. it assumes a yellow tint, which deepens through orange to brown as the temperature rises to 22° C. (71.6° F.), when the nitric peroxide enters into ebullition, yielding a reddish-brown vapor. This vapor also assumes a darker color as its temperature is raised, becoming at last almost black.

The vapor of nitric peroxide possesses a characteristic absorption spectrum.

These changes of color correspond to definite changes of molecular condition, as may be seen from a study of the vapor-density of nitric peroxide at different temperatures. At a temperature very little above its boiling point it possesses a vapor-density below that required for the formula $'\mathbf{N}^{iv}{}_2\mathrm{O}_4$, but nearer to this value than to that required for $'\mathbf{N}^{iv}\mathrm{O}_2$. As the temperature rises the vapor-density diminishes, till at 140° C. it corresponds exactly with the latter formula. There is, there-

fore, even at the boiling point of nitric peroxide, a partial dissociation of the larger molecules, $'\mathbf{N}^{iv}{}_2O_4$, into the smaller, $'\mathbf{N}^{iv}O_2$; but the greater number of the former still remain intact. The decrease in vapor-density corresponds with an increase in the relative number of dissociated molecules. It is probable that this dissociation begins even in the liquid state, as denoted by the change of color (see Note, p. 179).

Liquid nitric peroxide is a powerfully corrosive substance, and its vapor is very irritating when inhaled even in small quantity.

Reactions.—1. With metallic hydrates and oxides it yields a mixture of nitrite and nitrate in equivalent proportions:

$$\underset{\text{Nitric peroxide.}}{'\mathbf{N}^{iv}{}_2O_4} + \underset{\text{Potassic hydrate.}}{2\mathbf{O}KH} = \underset{\text{Potassic nitrate.}}{\mathbf{N}O_2Ko} + \underset{\text{Potassic nitrite.}}{\mathbf{N}OKo} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

It thus behaves like a compound anhydride—a view of its chemical character which is supported by its formation from nitric dioxychloride and argentic nitrite (see above).

2. A small quantity of water acts like a metallic hydrate, producing a mixture of nitrous and nitric acids:

$$\underset{\text{Nitric peroxide.}}{'\mathbf{N}^{iv}{}_2O_4} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Nitric acid.}}{\mathbf{N}O_2Ho} + \underset{\text{Nitrous acid.}}{\mathbf{N}OHo}.$$

But an excess of water decomposes it into nitric oxide and nitric acid:

$$\underset{\text{Nitric peroxide.}}{3'\mathbf{N}^{iv}{}_2O_4} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Nitric acid.}}{4\mathbf{N}O_2Ho} + \underset{\text{Nitric oxide.}}{2'\mathbf{N}''O}.$$

Composition.—The composition of nitric peroxide may be ascertained by passing the vapor of a known weight of the gas over red-hot metallic copper. The oxygen of the peroxide combines with the copper, and may be determined by ascertaining the increase in weight of the latter. The nitrogen is liberated, always mixed however with a small quantity of nitric oxide, and may be collected and measured. The proportion of nitric oxide must also be determined. From these data the composition of the peroxide may be calculated.

COMPOUNDS CONTAINING NITROGEN, CHLORINE, AND OXYGEN.

NITROUS OXYCHLORIDE, *Nitrosylic Chloride, Chloronitrous Gas.*

$\mathbf{N}OCl$.

Molecular weight = 65.5. *Molecular volume* $\square\square$. 1 *litre weighs* 32.75 *criths. Boils at* 0° C.

Preparation.—1. By the direct union of chlorine and nitric oxide:

$$\underset{\text{Nitric oxide.}}{2'\mathbf{N}''O} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Nitrous oxychloride.}\\\text{(Nitrosylic chloride.)}}}{2\mathbf{N}OCl}.$$

2. It is also evolved along with chlorine from a mixture of nitric and hydrochloric acids (see *Aqua-regia*, p. 218):

$$\underset{\text{Nitric acid.}}{\mathbf{N}O_2Ho} + \underset{\text{Hydrochloric acid.}}{3HCl} = \underset{\text{Nitrous oxychloride.}}{\mathbf{N}OCl} + \underset{\text{Water.}}{2\mathbf{O}H_2} + Cl_2.$$

Properties.—Nitrous oxychloride is an orange-colored gas, which, in a freezing-mixture, condenses to a red fuming liquid possessing an odor of aqua-regia.

Reactions.—1. Nitrous oxychloride is decomposed by water into nitrous and hydrochloric acids:

$$\underset{\text{Nitrous oxychloride.}}{\mathbf{N}OCl} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Nitrous acid.}}{\mathbf{N}OHo} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

In like manner it yields, with metallic oxides and hydrates, a mixture of nitrite and chloride:

$$\underset{\text{Nitrous oxychloride.}}{\mathbf{N}OCl} + \underset{\text{Potassic hydrate.}}{2\mathbf{O}KH} = \underset{\text{Potassic nitrite.}}{\mathbf{N}OKo} + \underset{\text{Potassic chloride.}}{KCl} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

Nitrous oxychloride belongs to the class of chlorides of the acid radicals, a view regarding its constitution which is expressed by the name *nitrosylic chloride.* These chlorides are derived from the corresponding acids by the substitution of chlorine for hydroxyl. Water decomposes them into the corresponding acid and hydrochloric acid, as in the foregoing reaction.

2. Nitrous oxychloride attacks mercury. The chlorine combines with the metal to form mercurous chloride, whilst nitric oxide is liberated:

$$\underset{\text{Nitrous oxychloride.}}{2\mathbf{N}OCl} + Hg_2 = \underset{\text{Mercurous chloride.}}{'\mathbf{Hg}'_2Cl_2} + \underset{\text{Nitric oxide.}}{2'\mathbf{N}''O.}$$

It is without action on gold or platinum.

The corresponding bromine compound, $\mathbf{N}OBr$, has also been prepared.

NITRIC DIOXYCHLORIDE, *Nitroxylic Chloride, Chloropernitric Gas.*

$$\mathbf{N}O_2Cl.$$

Molecular weight = 81.5. *Molecular volume* $\square\square$. 1 *litre weighs* 40.75 *criths. Boils at* 5° C. (41° F.).

Preparation.—1. By passing nitric peroxide and chlorine together through a heated glass tube:

$$\underset{\text{Nitric peroxide.}}{'\mathbf{N}^{iv}{}_2O_4} + Cl_2 = \underset{\substack{\text{Nitric dioxychloride.}\\\text{(Nitroxylic chloride.)}}}{2\mathbf{N}O_2Cl.}$$

2. By the action of chlorine on argentic nitrate as already described (see *Nitric Anhydride*, p. 219).

3. By the action of sulphuric dioxychlorhydrate (sulphurylic chlorhydrate) on nitric acid:

$$\underset{\text{Sulphuric dioxychlorhydrate.}}{\mathbf{S}O_2ClHo} + \underset{\text{Nitric acid.}}{\mathbf{N}O_2Ho} = \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} + \underset{\text{Nitric dioxychloride.}}{\mathbf{N}O_2Cl.}$$

4. It is most readily obtained by heating plumbic nitrate with phosphoric oxytrichloride:

$$\underset{\text{Plumbic nitrate.}}{3\left\{\begin{matrix}\mathbf{N}O_2\\ Pbo''\\ \mathbf{N}O_2\end{matrix}\right.} + \underset{\text{Phosphoric oxytrichloride.}}{2\mathbf{P}OCl_3} = \underset{\text{Triplumbic diphosphate.}}{\mathbf{P}_2O_2Pbo''_3} + \underset{\text{Nitric dioxychloride.}}{6\mathbf{N}O_2Cl.}$$

The action of the chlorine compounds of phosphorus on acids and their salts is a general method for the preparation of the chlorides of the acid radicals.

Properties.—Nitric oxychloride is a heavy yellow oil boiling at 5° C. (41° F.).
Reaction.—Water decomposes it into nitric and hydrochloric acids:

$$\begin{array}{ccccccc} NO_2Cl & + & OH_2 & = & NO_2Ho & + & HCl. \\ \text{Nitric dioxychloride.} & & \text{Water.} & & \text{Nitric acid.} & & \text{Hydrochloric acid.} \end{array}$$

Bases effect a similar decomposition, yielding a mixture of nitrate and chloride.

COMPOUNDS OF NITROGEN WITH HYDROGEN AND HYDROXYL.

AMMONIA.

NH_3.

Molecular weight = 17. *Molecular volume* $\square\square$. 1 *litre weighs* 8.5 *criths. Fuses at* —75° C. (—103° F.). *Boils at* —38.5° C. (—37.3° F.).

History.—The aqueous solution of ammonia was known to the alchemists. The gas was first obtained by Priestley, who also observed its decomposition by the electric spark. Berthollet first ascertained its composition.

Occurrence.—Ammonia occurs in small quantity in the air as carbonate, and in rain-water, especially in that which falls during thunderstorms, as nitrite and nitrate. Most fertile soils contain ammonia. As chloride and sulphate it is found in the neighborhood of active volcanoes. Along with boric acid, it occurs, as salts of ammonia, in the lagoons of Tuscany (p. 191), having probably been formed by the action of subterranean steam upon boric nitride:

$$\begin{array}{ccccccc} BN''' & + & 3OH_2 & = & BHo_3 & + & NH_3. \\ \text{Boric nitride.} & & \text{Water.} & & \text{Boric acid.} & & \text{Ammonia.} \end{array}$$

It also occurs, in the form of its salts, in animal fluids, particularly in putrid urine, and in the juices of plants.

Formation.—Ammonia is formed: 1. By the decay of animal and vegetable matters containing nitrogen. It is from this source that the atmospheric ammonia is derived.

2. By the destructive distillation of these nitrogenous matters. The ammonia of commerce is thus obtained. Formerly, horn, hoofs, and bones were distilled for this purpose, and hence the name *spirits of hartshorn* was given to ammonia; but its chief source at the present day is the ammoniacal liquor of gas works, in which it occurs as a by-product from the distillation of coal. Volcanic ammonia is also a product of the destructive distillation of nitrogenous vegetable matter, being formed only where the lava has flowed over fertile soil.

3. By the action of nascent hydrogen (from zinc and caustic alkali) on nitric and nitrous acids.

4. Ammonia is also formed synthetically from its elements when the silent electric discharge is passed through a mixture of nitrogen and hydrogen (Donkin).

Preparation.—Ammonia may be prepared from any of its salts by

heating these with slaked lime. The chloride is usually employed for this purpose:

$$2NH_4Cl \quad + \quad CaHo_2 \quad = \quad CaCl_2 \quad + \quad 2NH_3 \quad + \quad 2OH_2.$$

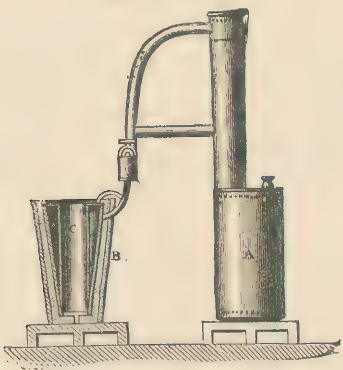
$2NH_4Cl$	$CaHo_2$	$CaCl_2$	$2NH_3$	$2OH_2$
Ammonic chlóride.	Calcic hydrate.	Calcic chloride.	Ammonia.	Water.

One part of ammonic chloride is mixed with 2 parts of slaked lime in powder, and the whole is heated in a flask. If gaseous ammonia is required, the gas evolved may be dried by passing over quicklime (calcic chloride absorbs gaseous ammonia), and may be collected either over mercury or by upward displacement. When an aqueous solution is required the gas is passed direct into water, which is contained in a series of Woulff's bottles fitted with safety-tubes. The delivery tubes must pass to the bottom of the liquid, otherwise only the upper layer would be saturated, as the aqueous solution of ammonia is lighter than water.

Properties.—Ammonia is a colorless gas, with a very pungent odor. Its density is 0.589 (air = 1). It turns red litmus blue, and yellow turmeric paper brown. It neutralizes acids, uniting directly with them to form salts (see *Reactions*).

Ammonia may be liquefied by cold or pressure. Faraday first obtained it in the liquid state by heating argentic ammonio-chloride in one limb of a bent sealed tube, whilst the other was immersed in a freezing mixture. The argentic ammonio-chloride is prepared by passing ammonia over dry argentic chloride, which in this way absorbs 320

FIG. 38.



times its volume of the gas. The double compound parts with all its ammonia when heated to 112° C. (233.6° F.). By conducting the heating in a bent sealed tube as above described, the ammonia is liquefied by the joint action of its own pressure, and of the cold of the freezing mixture. Calcic ammonio-chloride may be substituted for the argentic compound in the above experiment. Ammonia may also be liquefied by the action of cold alone at a temperature of —40° to —50° C. (—40° to —57° F.), by passing the gas through a tube immersed in a mixture of ice and crystallized calcic chloride.

Liquid ammonia is a mobile, colorless, highly refracting liquid, boiling at —38.5° C. (—37.3° F). At —10° C. (14° F.) it has a sp. gr. of 0.65. When subjected to a temperature below —75° C. (—103° F.) it solidifies to a white crystalline translucent mass.

The cold produced by the rapid evaporation of liquid ammonia has been utilized in Carré's apparatus for the artificial production of ice. Two strong wrought-iron vessels, *A* and *B* (Fig. 38), are connected by a tube of the same material. *A* contains an aqueous solution of ammonia saturated at 0° C. When ice is to prepared by means of this apparatus, heat is applied to *A*, whilst *B* is immersed in cold water. Gaseous ammonia is evolved from *A*, and condenses under its own pressure between the double walls of the receiver *B*. When a sufficient quantity of the gas has been driven off, *A* is cooled by means of water, whilst the water to be frozen is introduced into a metal cylinder, *C*, into the cavity of the receiver *B*, the space between receiver and cylinder being filled with alcohol, which does not freeze, and serves as a conducting medium. As the liquid in *A* cools, it rapidly reabsorbs ammonia, which boils off from *B* as fast as the pressure is removed, producing a great depression of temperature by means of the heat which becomes latent, and freezing the water contained in the metal cylinder.

Ammonia is exceedingly soluble in water. Water at 0° C. absorbs more than 1100 times its volume of the gas, evolving great heat in the process. When the ammonia is pure, the absorption is instantaneous, the water rushing into the space occupied by the gas as into a vacuum. The affinity of the two substances for each other is nevertheless slight, as the solubility of ammonia in water decreases rapidily at higher temperatures, and the gas is completely expelled from the liquid by boiling. When exposed to the air, the aqueous solution also parts with nearly all its gas by diffusion. When ammonia is removed in the gaseous state from its solution, the heat which was liberated during the process of solution is again absorbed: thus by sending a rapid current of air from a foot blower through concentrated aqueous ammonia, the gas is expelled, and the temperature sinks below —40° C. (—40° F.).

Specific Gravity Table of Aqueous Ammonia at 14° *C.*

d.	*p.*	*d.*	*p.*
0.8844	36	0.9347	17
0.8864	35	0.9380	16
0.8885	34	0.9414	15
0.8907	33	0.9449	14
0.8929	32	0.9484	13
0.8953	31	0.9520	12
0.8976	30	0.9555	11
0.9001	29	0.9593	10
0.9026	28	0.9631	9
0.9052	27	0.9670	8
0.9078	26	0.9709	7
0.9106	25	0.9749	6
0.9133	24	0.9790	5
0.9162	23	0.9831	4
0.9191	22	0.9873	3
0.9221	21	0.9915	2
0.9251	20	0.9959	1
0.9283	19	0.9975	0.6
0.9314	18	0.9991	0.2

The foregoing table (Carius) gives the specific gravity of the aqueous solutions of ammonia of various strengths at 14° C. (57.2° F.). The column d contains the specific gravities, the column p the corresponding percentages of ammonia.

Ammonia does not support combustion and does not burn in air unless the latter be heated. When mixed with oxygen, however, it is readily inflammable, burning with a pale yellow flame.

At a bright red heat ammonia is decomposed into its elements. This decomposition, which is best effected by electric sparks, affords a means of ascertaining the composition of the gas.

Reactions.—1. Ammonia is decomposed by chlorine (see p. 212). Bromine and iodine have a similar action. Under certain conditions, when chlorine and iodine are employed in excess, the explosive compounds, nitrous chloride and nitrous iodide (*q.v.*) are formed.

2. When ammonia is passed over charcoal heated to redness in a tube, ammonic cyanide is formed and hydrogen is evolved:

$$\underset{\text{Ammonia.}}{2\mathbf{N}H_3} + C = \underset{\text{Ammonic cyanide.}}{\mathbf{N}^{v}H_4(CN)} + H_2.$$

3. The metals of the alkalies, when heated in gaseous ammonia, replace the hydrogen atom for atom:

$$\underset{\text{Ammonia.}}{\mathbf{N}H_3} + Na = \underset{\text{Sodic amide.}}{\mathbf{N}NaH_2} + H.$$

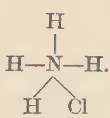
4. Ammonia unites directly with acids, forming the ammonium salts, in which the atomicity of nitrogen is ^{v}:

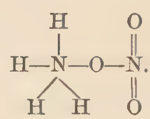
$$\mathbf{N}'''H_3 + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Ammonic chloride.*}}{\mathbf{N}^{v}H_4Cl.}$$

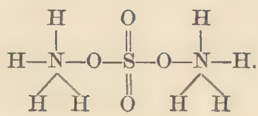
$$\mathbf{N}'''H_3 + \underset{\text{Nitric acid.}}{\mathbf{N}^{v}O_2Ho} = \underset{\text{Ammonic nitrate.†}}{\mathbf{N}^{v}O_2(N^{v}H_4O).}$$

$$2\mathbf{N}'''H_3 + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} = \underset{\text{Ammonic sulphate.‡}}{\mathbf{S}O_2(N^{v}H_4O)_2.}$$

When a glass rod moistened with hydrochloric acid is brought close to a liquid evolving ammonia, white fumes of ammonic chloride are

* 

† 

‡ 

formed. If the ammonia is in combination, the substance must be warmed with a solution of caustic alkali before applying this test.

Ammonic chloride forms with platinic chloride a yellow crystalline double salt of the formula $\mathbf{PtCl_4,2NH_4Cl}$, almost insoluble in water, and insoluble in alcohol or ether. This salt is employed in the quantitative determination of ammonia.

Composition.—The composition of ammonia may be ascertained in the following manner. A measured volume of gaseous ammonia is introduced into an eudiometer tube over mercury. The tube is furnished with platinum wires fused into the glass for the purpose of passing the electric spark, which is furnished by an induction coil. The spark is allowed to pass through the gas as long as any increase of volume is observed. The resulting mixture of gases is then measured; an excess of oxygen is added, and the whole is exploded by means of the spark. Two-thirds of the contraction which follows the explosion represents the volume of hydrogen contained in the mixture. The following example will illustrate the use of this method:

The mixture of gases resulting from the decomposition of 100 cubic centimetres of ammonia is found to measure	200 c.c.
Add 100 c.c. of oxygen, ...	100 c.c.
Total, ...	300 c.c.
After explosion there remain	75 c.c.
Contraction, ...	225 c.c.

The hydrogen contained in the 200 c.c. is therefore $\frac{2}{3} \times 225 = 150$ c.c., and the nitrogen is $200 - 150 = 50$ c.c.; the two gases are therefore present in the proportion of 3 volumes of hydrogen to 1 volume of nitrogen. Further, as the mixed gases occupied twice the volume of the ammonia, it is evident that these 4 volumes in combining have undergone the normal condensation to 2 volumes. Expressing the volumes in litres:

1 litre of nitrogen weighs	14 criths.
3 litres of hydrogen weigh	3 "

The proportion by weight in which these elements are combined is therefore, 14 parts by weight of nitrogen to 3 of hydrogen. Dividing each of these numbers by the atomic weight of the corresponding element, the atomic proportion 1 : 3, represented by the formula $\mathbf{NH_3}$, is arrived at.

AMMONIUM.

$$\left\{\begin{matrix}\mathbf{N}H_4\\ \mathbf{N}H_4\end{matrix}\right.$$

This monad radical has never been obtained in the free state, but its compounds are perfectly analogous, in crystalline form and other properties, to those of potassium. These facts have led some chemists to consider the group $\mathbf{N}H_4$ as a metal, to which they have given the name ammonium, a hypothesis which is considered to receive support from the production of an unstable amalgam of this radical. All the compounds of mercury with metals are found to possess metallic lustre; and this is the case with the amalgam of ammonium. It may be prepared by two different processes.

1. If a solution of ammonic chloride be electrolyzed, the negative electrotrode being mercury and the positive a platinum plate, the mercury is observed to swell up owing to the formation of a spongy metallic mass. The solution ought to contain an excess of ammonia, otherwise the explosive compound, nitrous chloride, may be formed at the positive electrode.

2. On pouring into a slightly warmed solution of ammonic chloride an amalgam of potassium or sodium, the amalgam is found to swell enormously, owing to its conversion into ammonium amalgam, whilst potassic or sodic chloride is simultaneously formed:

$$\underset{\text{Sodic amalgam.}}{Hg_nNa_m} + \underset{\text{Ammonic chloride.}}{m\mathbf{N}H_4Cl} = \underset{\text{Ammonium amalgam.}}{Hg_n(\mathbf{N}^vH_4)_m} + \underset{\text{Sodic chloride.}}{mNaCl.}$$

Ammonium amalgam rapidly decomposes into mercury, ammonia, and hydrogen, the ammonia and hydrogen being liberated in the proportion of $2\mathbf{N}H_3$ to H_2:

$$\underset{\text{Ammonium amalgam.}}{2Hg_n(\mathbf{N}^vH_4)_m} = \underset{\text{Mercury.}}{2nHg} + \underset{\text{Ammonia.}}{2m\mathbf{N}H_3} + mH_2.$$

Ammonium plays the part of a compound monad radical, and its salts are isomorphous with those of potassium; they are all volatile, unless the acid from which they are derived is fixed. They will be more fully described along with the metals of the alkalies.

HYDROXYLAMINE.

$$\mathbf{N}H_2Ho.$$

This remarkable compound, which was discovered by Lossen, may be regarded as ammonia in which one atom of hydrogen has been displaced by hydroxyl.

Preparation.—1. Hydroxylamine is formed by the direct union of nitric oxide with nascent hydrogen:

$$\underset{\text{Nitric oxide.}}{2'\mathbf{N}''O} + 3H_2 = \underset{\text{Hydroxylamine.}}{2\mathbf{N}H_2Ho.}$$

Nitric oxide is passed into a mixture in which hydrogen is being generated—thus into a flask containing tin and dilute hydrochloric acid.

2. Nitric and nitrous acids also yield hydroxylamine when added to the above reducing mixture:

$$\underset{\text{Nitric acid.}}{\mathbf{N}O_2Ho} + 3H_2 = \underset{\text{Hydroxylamine.}}{\mathbf{N}H_2Ho} + \underset{\text{Water.}}{2\mathbf{O}H_2.}$$

In these reactions the hydroxylamine remains in solution combined with the hydrochloric acid.

Properties.—Free hydroxylamine is known only in its aqueous solution, which is colorless, devoid of odor, and powerfully alkaline. On distilling the solution, part of the base passes over with the steam, but the greater part is decomposed with formation of ammonia. The solution possesses reducing properties and precipitates silver and mercury in the metallic state from the solutions of their salts.

Hydroxylamine is a mon-acid base. Its salts, which crystallize well, are formed, like those of all amine bases, by the direct union of base and acid without elimination of water.

COMPOUNDS OF NITROGEN WITH CHLORINE, BROMINE, AND IODINE.

NITROUS CHLORIDE.

$\mathbf{N}Cl_3$?

Preparation.—Nitrous chloride is formed when chlorine is passed into a solution of ammonic chloride warmed to about 30° C.:

$$\mathbf{N}^{v}H_4Cl + 3Cl_2 = \mathbf{N}'''Cl_3 + 4HCl.$$

The same reaction takes places when a solution of ammonic chloride is electrolyzed, the chlorine which is evolved at the positive electrode acting on the ammonium salt.

Properties.—Nitrous chloride is a yellow oil, of specific gravity 1.6, possessing a disagreeable, pungent odor. Its vapor irritates the eyes.

Nitrous chloride is the most dangerously explosive substance known. A slight rise of temperature, or the mere contact with certain bodies—such as fats, phosphorus, or arsenic—is sufficient to cause it to decompose instantaneously with explosive violence into its elements. Very frequently explosion occurs without apparent cause.

Ammonia decomposes it with formation of ammonic chloride and liberation of nitrogen. Its formation is therefore prevented by the presence of an excess of ammonia (see *Nitrogen*, p. 213).

The formula of this compound has not been ascertained with certainty: it may contain hydrogen, and it is possible that the compounds intermediate between ammonia and nitrous chloride may exist:

$$NH_3,\quad NH_2Cl,\quad NHCl_2,\quad NCl_3.$$

NITROUS BROMIDE.

NBr_3?

This compound is obtained as a dark-red, very explosive oil by adding an aqueous solution of sodic or potassic bromide to nitrous chloride:

$$\underset{\text{Nitrous chloride.}}{NCl_3} + \underset{\text{Potassic bromide.}}{3KBr} = \underset{\text{Nitrous bromide.}}{NBr_3} + \underset{\text{Potassic chloride.}}{3KCl.}$$

NITROUS IODIDE.

NI_3.

When aqueous or alcoholic ammonia is poured on finely powdered iodine, a black substance is formed which is highly explosive, and, when dry, detonates on the slightest touch. The product varies in composition, according as aqueous or alcoholic ammonia is employed. A nitrous hydrodiniodide is formed at the same time:

$$\underset{\text{Ammonia.}}{4NH_3} + 3I_2 = \underset{\text{Nitrous iodide.}}{NI_3} + \underset{\text{Ammonic iodide.}}{3NH_4I.}$$

$$\underset{\text{Ammonia.}}{3NH_3} + 2I_2 = \underset{\text{Nitrous hydrodiniodide.}}{NHI_2} + \underset{\text{Ammonic iodide.}}{2NH_4I.}$$

THE ATMOSPHERE.

The atmosphere of the earth consists of a mixture of gaseous, liquid, and solid matters. The chief gaseous constituents are nitrogen, oxygen, a small quantity of carbonic anhydride, and a varying proportion of aqueous vapor. Water also occurs in the liquid state in minute particles in the form of mist. The solid matters consist of ice particles, volcanic and other dust, sporules and metallic salts—notably sodic chloride—in a finely divided state.

The atmosphere is generally considered to extend to a height of about 45 miles above the earth's surface, this estimate being based upon observations of the length of time during which the twilight is visible in the zenith. Meteorites, however, ignite at an elevation of about 200

miles, proving the presence of a medium which, though of too great tenuity to reflect light, still possesses density, and offers resistance to the passage of bodies through it. It is probable that even this height does not denote the upper limit of the atmosphere.

Owing to the effect of gravitation and the elasticity of the atmosphere, the lower strata have a much greater density than the higher strata. If the density, instead of thus gradually decreasing with the elevation, were uniform throughout, and identical with that which prevails at the earth's surface, the entire height of the atmosphere would be only about 5 miles. This diminution of density is such that at a height of about 3 miles the barometric pressure is only half as great as at the earth's surface, and consequently one-half of the atmosphere lies below this height.

According to the very accurate determinations of Regnault the weight of 1 litre of pure dry air at 0° C., and under a pressure of 760 millimetres of mercury (the average barometric pressure at the level of the sea—a pressure commonly referred to as that of 1 atmosphere) in the latitude of Paris, is 1.2932 grams. Air is thus 773 times lighter than water, 10,500 times lighter than mercury, and 14.45 times heavier than hydrogen. A column of the height of the atmosphere and of 1 inch square weighs 15 lbs. Thus 27,000,000 tons rest upon every square mile of the earth's surface.

The luminous rays of the sun pass through the atmosphere without appreciably heating it, except in so far as they are intercepted and absorbed by suspended solid or liquid matter; but the rise of temperature from the latter cause is not great. The dark heat-rays, however, are partly absorbed, and this absorption is due to aqueous vapor. These dark rays represent, however, but a fraction of the total radiant energy of the sun, of which the greater part therefore reaches the earth unimpaired. Here both the visible and the invisible rays are converted by absorption into heat; and radiation from the earth's surface in the form of dark heat is for the most part intercepted by aqueous vapor. In this way, the earth which has been heated by the sun imparts its heat to the air immediately resting upon it, and the aqueous vapor acts as a trap for the solar rays, allowing them to enter freely in the form of luminous heat, but preventing their escape when they are once converted into dark heat. Thus a too rapid cooling of the earth's surface during the absence of the sun, and the consequent great inequalities of temperature, are prevented. The air, thus heated by contact with the earth, expands, and, becoming lighter, rises, and shares its heat with the strata above, whilst air from some colder quarter flows in to supply its place. The air is thus in constant motion, and differences in composition of the atmosphere in various places, which might arise from local causes, are prevented. To this heating and cooling, and to the varying quantities of aqueous vapor present in hot and in cold air, the variations of the barometric pressure are due. Equalization of temperature is also effected by the condensation of aqueous vapor during a fall of temperature, the latent heat of vaporization being recovered in this process.

The highest atmospheric temperature (temperature in shade) that has

been observed is about 49° C. (120.2° F.); the lowest —49° C. (—56.2° F.).

The expansion of air by heat is 0.003665 of its volume measured at 0° C. for every 1° above 0° C.

As regards the chemical composition of the atmosphere, the proportion of oxygen to nitrogen is nearly constant; the proportions of the other constituents are subject to considerable variation. The following table contains determinations of the relative quantities of oxygen and nitrogen present in dry air freed from carbonic anhydride. As is usual in the analysis of gaseous mixtures, the results are expressed in parts by volume.

Composition of Atmospheric Air from various Localities. In 100 *parts by volume.*

	Oxygen. Parts by volume.	Nitrogen. Parts by volume.
St. Bartholomew's Hospital,	20.885	79.115
	20.999	79.001
Paris,	20.913	79.087
	20.999	79.001
Lyons,	20.918	79.082
	20.966	79.034
Toulon,	20.912	79.088
	20.982	79.018
Berlin,	20.908	79.092
	20.998	79.002
Madrid,	20.916	79.084
	20.982	79.018
Geneva,	20.909	79.091
	20.993	79.007
Montanvert,	20.963	79.037
Summit of Pichincha, 16,000 ft.	20.949	79.051
	20.988	79.012
North American Prairie,	20.910	79.090
South America,	20.960	79.040
Liverpool to Vera Cruz,	20.918	79.082
	20.965	79.035
18,000 ft. above London,	20.885	79.115
Manchester,	20.876	79.124
	20.888	79.112
Algiers (June 5, 1851),	20.420	79.580
	20.395	79.605
Bay of Bengal (Feb. 1, 1849),	20.460	79.540
	20.450	79.550
Ganges (March 8, 1849),	20.387	79.613
	20.390	79.610

These analytical results, except in the case of the three localities last mentioned, display a remarkable uniformity. The cause of the variation in the case of the sample from Algiers is unexplained; but as re-

gards the sample from the Bay of Bengal and the Ganges, it is to be noted that these were collected during an outbreak of cholera when the water contained large quantities of putrefying organic matter.*

The presence of a very small quantity of the oxygen as ozone has already been referred to (p. 166).

The average proportion of carbonic anhydride present in air is about 0.03 per cent.; but the amount may vary considerably owing to local causes. Thus the effect of animal life is to increase the proportion of carbonic anhydride; that of vegetable life to diminish it (see p. 202). In putrefaction and in combustion, large quantities of this gas are given off. In London, combustion and respiration daily send into the air at least 200,000,000 cubic feet of carbonic anhydride. Each ton of coal consumed furnishes about 3 tons of carbonic anhydride, and abstracts 2.75 tons of oxygen from the air. The variations due to the above causes are very noticeable: thus in crowded and ill-ventilated rooms, the air may contain as much as 0.3 per cent. of carbonic anhydride; air from the centre of London contains 0.11 per cent. Near the surface of the ocean, both oxygen and carbonic anhydride are slightly in excess during the day, and slightly deficient during the night. This is due to the fact that these gases are more soluble in water than nitrogen: in the night time the cold water dissolves them in larger quantity, and this dissolved excess is again expelled when the water is heated by the sun's rays during the day. At great altitudes the proportion of carbonic anhydride appears to increase: thus the air at the Grands Mulets was found to contain 0.1 per cent.

The proportion of aqueous vapor present in the air varies greatly. The maximum quantity of aqueous vapor which a given volume of air can take up is constant for a given temperature, and independent of the pressure. When air has taken up this maximum quantity it is said to be *saturated* with moisture. The amount necessary for saturation at a given temperature can be calculated from the tension of the vapor of water for that temperature. In this way it is found that 1 cubic metre of air can take up the following weights of aqueous vapor:

At 0° C. (32° F.),	4.871 grams.
At 10° C. (50° F.),	9.362 grams.
At 20° C. (68° F.),	17.157 grams.
At 30° C. (86° F.),	30.095 grams.
At 40° C. (104° F.),	50.700 grams.

The air is very seldom saturated with moisture. When the temperature of air containing aqueous vapor falls, as soon as the point is passed at which the quantity of aqueous vapor present corresponds to saturation, a separation of the excess of this vapor in the form of mist, rain, snow, or hail begins. This point is known as the dew-point, and by

* The oxygen in the foregoing samples was determined by exploding the air with hydrogen and noting the contraction. If, as is quite conceivable, the air in the above abnormal cases contained traces of marsh-gas derived from the decomposition of organic matter, a smaller contraction would be observed, and the percentage of oxygen would be found too low.

determining it accurately, the quantity of aqueous vapor present in incompletely saturated air may be ascertained. The usual proportion by volume of aqueous vapor in air, varies from 0 to 5 per cent.

The question of the proportion of aqueous vapor present in air is of great importance in meteorology; but in the chemical examination of air the aqueous vapor is taken into account only in so far as by its volume it diminishes the absolute quantity of the other constituents present in a given bulk. It is usual, in the analyses of gases, to eliminate the aqueous vapor from the result by calculation.

Other constituents of the air, which are, however, present only in minute quantity, are salts of ammonia, namely, the carbonate, nitrate, and nitrite. Ammonia is given off in the putrefaction of animal and vegetable matter. Oxides of nitrogen are formed whenever a flash of lightning passes through air: rain-water, especially if collected after a thunderstorm, contains nitrates and nitrites. The presence of these nitrogenous compounds in the air is of great importance to plant life, as it is from this source alone that plants which have not been supplied with a nitrogenous manure obtain the nitrogen necessary for their growth. Plants cannot assimilate free nitrogen.

Another product of putrefaction which is constantly being given off into the air is marsh-gas. It is doubtful, however, whether the presence of this compound in air has been proved, except in the neighborhood of putrefying matter.

Although the various gases which together make up the atmosphere possess very different specific gravities, they display no tendency to separate from each other. On the contrary, by the laws of diffusion, any number of gases which are brought into contact have a tendency to become thoroughly mixed, even although there are no actual currents in the gases, and even although the lighter gases may be uppermost at the commencement of the process. The influence of currents of air in preserving uniformity of composition has already been referred to.

As regards the suspended matter in the atmosphere, this may, as already stated, be both solid and liquid. These particles, even when present in small quantity, are rendered visible to the eye by their property of reflecting light: thus when a ray of light passes through a dark room, the path of the ray appears luminous. By filtration through cotton wool, or by subsidence, the particles are removed, and the path of a ray of light through air thus purified ceases to be visible. These particles are never absent from air under ordinary conditions. When solid particles are present in quantity sufficient to obstruct visibly the passage of light, they constitute a dust-haze. Piazzi Smyth observed a strong dust-haze on the summit of the Peak of Teneriffe at an altitude of 12,000 feet. Minute liquid particles constitute ordinary mist or fog. When the surface of the sea is violently agitated by the wind, particles of sea-water are thrown into the air in the form of spray: these are carried far inland by the wind, yielding by evaporation solid particles of sea salt, a substance which is scarcely ever absent from air. The yellow flashes which a Bunsen flame emits from time to time, while burning in air, are due to sodium compounds, as may be proved by spectroscopic examination. In the neighborhood of the sea

the quantity of sodic chloride present in air is of course greater than further inland. At Land's End for example, the rain water contains as much as 0.033 per cent. of this salt. At great altitudes in Switzerland the air almost always contains minute particles of snow, which may be seen by putting the eye in shadow and looking into sunshine. Among the organic solid particles present in air, are to be reckoned the germs of putrefactive and other fermentations. This is shown by the fact that air which has been effectually freed from all suspended matter by filtration does not induce putrefaction in milk, flesh, urine, and other readily alterable animal substances, however long these may be left in contact with it.

If a Bunsen flame be placed under the path of a ray of light in a dark room, the heated air rising from the flame appears like a black smoke, owing to the absence of suspended matter in the products of combustion. The same phenomenon may be shown, though in a less striking manner, by substituting for the flame a flask filled either with oil heated to 120°–130° C. (248°–266° F.), or with ice-cold water, and concentrating the ascending or descending current of air upon the path of the ray by means of a conical paper funnel. This phenomenon has not yet received any satisfactory explanation.

It has been shown by Lodge that the electrification of air also rapidly removes the suspended particles contained in it.

That the oxygen and nitrogen, which form the chief constituents of the atmosphere, are present in a state of mere mechanical mixture and not, as was formerly supposed, in chemical combination, is proved by a variety of considerations. Thus the proportion by volume of the two gases to each other is highly complex, 21 volumes of oxygen to 79 volumes of nitrogen being the simplest proportion that can be assumed; whereas in compounds of only two elements much simpler relations prevail. No contraction occurs when oxygen and nitrogen form air, and there is no case known in which two gases unite chemically in unequal proportions by volume without contraction. When oxygen and nitrogen are mixed in the above proportions, no heat is evolved, nor is there any other sign of chemical combination; nevertheless, the mixture displays all the properties of air. When air is dissolved in water, the proportion of its constituents is totally altered, owing to the greater solubility of oxygen; thus, dissolved air contains, in 100 volumes, 32.5 volumes of oxygen and 67.5 volumes of nitrogen. Again, air which has been forced through a thin caoutchouc membrane contains 41.6 volumes of oxygen to 58.4 volumes of nitrogen, owing to the property which oxygen possesses of passing more readily through caoutchouc. If air were a chemical compound, the proportion of its constituents could not be thus altered by solution or by osmosis.

CHAPTER XXVII.

HEXAD ELEMENTS.

SECTION I.

SULPHUR, S_2.

Atomic weight = 32. *Molecular weight* = 64. *Molecular volume* ☐☐ *at* 1000° C., *but only one-third of this at its boiling-point.* 1 *litre of sulphur vapor weighs* 32 *criths. Rhombic variety fuses at* 114.5° C. (238.1° F.). *Boils at* 445° C. (833° F.). *Atomicity* $''$, ^{iv}, *and* ^{vi}. *Evidence of atomicity:*

Sulphuretted hydrogen, ...	$S''H_2$.
Triethylsulphinic iodide, ...	$S^{iv}Et_3I$.
Sulphuric oxydichloride (*Sulphurylic chloride*), ...	$S^{vi}O_2Cl_2$.
Sulphuric iodide, ...	$S^{vi}I_6$.
Sodic dinitrosulphate, ...	$S^{vi}O(NO)_2Nao_2$.

History.—This element has been known from the earliest historical times.

Occurrence.—Sulphur occurs both native and in combination. Native sulphur is found chiefly in the neighborhood of volcanoes: thus in Sicily, whence the greater part of the native sulphur of commerce is obtained. In combination it occurs either with metals alone as sulphides, or with metals and oxygen as sulphates. Of the former the most important as sources of sulphur are ferric disulphide or iron pyrites ($\mathbf{Fe}S''_2$) and copper pyrites ($Fe_2Cu_2S_4$). The sulphides of zinc, lead, mercury, and antimony are important ores of these metals. The most commonly occurring sulphates are calcic sulphate—which is found in two forms, as gypsum ($\mathbf{S}Ho_4Cao''$), and as anhydrite ($\mathbf{S}O_2Cao''$)—baric sulphate, or heavy spar ($\mathbf{S}O_2Bao''$), and magnesic sulphate, which also occurs in two forms, as kieserite ($\mathbf{S}OHo_2Mgo''$), and as Epsom salts ($\mathbf{S}OHo_2Mgo'',6\mathbf{O}H_2$). The sulphates of calcium, magnesium, and sodium occur in natural waters. Of gaseous compounds, both sulphurous anhydride ($\mathbf{S}O_2$) and sulphuretted hydrogen ($\mathbf{S}H_2$) are of frequent occurrence in volcanic exhalation, the latter being also found in many mineral waters. Sulphur is a constituent of many complex organic compounds in the animal and vegetable kingdoms.

Formation of Volcanic Sulphur.—This is probably due to the mutual decomposition of the two volcanic gases, sulphurous anhydride and sulphuretted hydrogen, in presence of water. In this reaction pentathionic acid and water are formed, whilst sulphur is liberated:

$$\underset{\text{Sulphurous anhydride.}}{5\mathbf{S}O_2} + \underset{\text{Sulphuretted hydrogen.}}{5\mathbf{S}H_2} = \underset{\text{Pentathionic acid.}}{\left\{\begin{array}{l}\mathbf{S}O_2Ho\\(S''_3)''\\\mathbf{S}O_2Ho\end{array}\right.} + \underset{\text{Water.}}{4\mathbf{O}H_2} + 5S.$$

Manufacture.—1. Native sulphur is usually mixed with large quantities of earthy matters, from which it is separated by fusion. In Sicily, the heat for this purpose is obtained by the combustion of a portion of the sulphur itself. The sulphur ore is built up into a large heap over a pit sunk into the ground. The heap is ignited from beneath, and as the heat slowly penetrates through the mass, the sulphur melts and flows into the pit, which is so arranged that the liquid product can be drawn off during the process. By this method more than half the sulphur burns away as sulphurous anhydride.

2. Sulphur is also obtained by distilling iron pyrites:

$$\underset{\text{Ferric disulphide.}}{3\mathbf{Fe}S_2} = \underset{\text{Triferric tetrasulphide.}}{{}^{iv}(\mathbf{Fe}_3)^{viii}S_4} + S_2.$$

The reaction is analogous to that which takes place in the preparation of oxygen from manganic peroxide (p. 161). The distillation is performed in fire-clay cylinders. It is, however, in every way more economical to burn the pyrites in kilns, a method which has been generally adopted. The kiln is lighted from below; part of the sulphur which, in the process of distillation in cylinders, remains in combination with the iron, burns, forming sulphurous anhydride; the remainder distils off and is condensed. The exhausted pyrites is from time to time withdrawn from the lower part of the kiln, and a fresh charge is introduced at the top, thus rendering the process more continuous. By this method one-half of the total sulphur is obtained from the pyrites:

$$\underset{\text{Ferric disulphide.}}{3\mathbf{Fe}S_2} + 5O_2 = \underset{\text{Triferric tetroxide.}}{{}^{iv}(\mathbf{Fe}_3)^{viii}O_4} + \underset{\text{Sulphurous anhydride.}}{3\mathbf{S}O_2} + 3S.$$

By passing the products through heated charcoal a larger yield can be obtained.

Sulphur is obtained in a similar manner from copper pyrites in the process of roasting the ore in the first stage of copper-smelting.

3. The *alkali-waste* obtained in the manufacture of sodic carbonate (*q.v.*) may be made to yield considerable quantities of sulphur. This waste, which remains after the extraction of the sodic carbonate from the *black-ash* by lixiviation, consists essentially of insoluble calcic oxysulphide, a combination of calcic sulphide with calcic oxide in varying proportions. Without removing the waste from the lixiviating vats, a current of air is blown through it, by which means the calcic sulphide contained in the oxysulphide is oxidized with considerable rise of temperature, yielding a mixture of soluble polysulphides of calcium and calcic thiosulphate:

$$(a.)\ \underset{\text{Calcic sulphide.}}{2\mathbf{Ca}S} + O + \underset{\text{Water.}}{OH_2} = \underset{\text{Calcic disulphide.}}{\mathbf{Ca}(S''_2)''} + \underset{\text{Calcic hydrate.}}{\mathbf{Ca}Ho_2}.$$

$$(b.)\ \underset{\text{Calcic disulphide.}}{\mathbf{Ca}(S''_2)''} + 3O = \underset{\text{Calcic thiosulphate.}}{\mathbf{S}O_2\left(\begin{matrix}O\\S\end{matrix}\mathbf{Ca}\right)''}.$$

Calcic sulphide is also liberated from its combination with the lime and becomes soluble. The oxidation is allowed to proceed till one-half of the sulphur has been converted into thiosulphate, and the remainder into calcic sulphide or polysulphide, after which the whole is lixiviated, and the solution treated with hydrochloric acid. The sulphur is liberated, as represented by the following equation :

$$\underset{\text{Calcic sulphide.}}{2\mathbf{Ca}S} + \underset{\text{Calcic thiosulphate.}}{SO_2\left(\begin{matrix}O\\S\end{matrix}Ca\right)''} + \underset{\text{Hydrochloric acid.}}{6HCl} = 4\dot{S} + \underset{\text{Calcic chloride.}}{3\mathbf{Ca}Cl_2} + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

Calcic polysulphides undergo an analogous decomposition with calcic thiosulphate when treated with hydrochloric acid, but the quantity of sulphur liberated is proportionately larger.

The sulphur thus obtained is melted under superheated water.

4. Sulphur is obtained in the purification of coal-gas. The crude gas contains sulphuretted hydrogen. In order to remove this impurity, the gas is passed through ferric hydrate, which absorbs the sulphuretted hydrogen with formation of ferrous sulphide and separation of sulphur :

$$\underset{\text{Ferric hydrate.}}{\mathbf{Fe}_2Ho_6} + \underset{\text{Sulphuretted hydrogen.}}{3\mathbf{S}H_2} = \underset{\text{Ferrous sulphide.}}{2\mathbf{Fe}S} + S + \underset{\text{Water.}}{6\mathbf{O}H_2}.$$

When the mixture has lost its absorptive power, it is exposed to the air in a moist state, ferric hydrate being thus regenerated and sulphur set free:

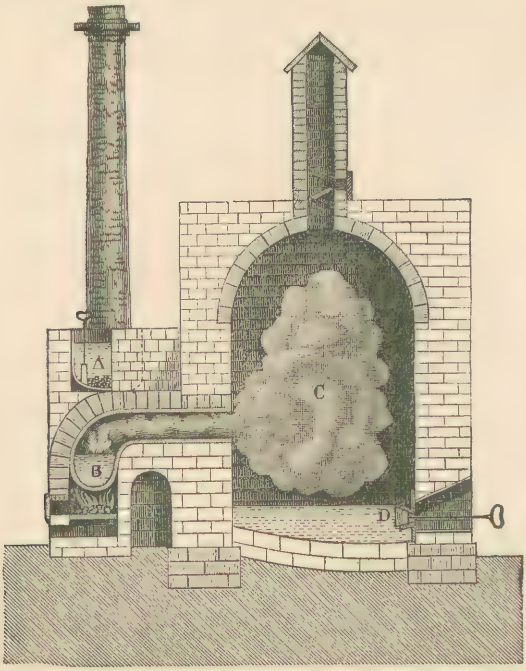
$$\underset{\text{Ferrous sulphide.}}{2\mathbf{Fe}S} + \underset{\text{Water.}}{3\mathbf{O}H_2} + 3O = \underset{\text{Ferric hydrate.}}{\mathbf{Fe}_2Ho_6} + S_2.$$

In this condition the mixture is again employed in the removal of sulphuretted hydrogen. These alternate processes of absorption and oxidation are repeated till the mixture contains half its weight of sulphur, when the latter is separated by distillation.

Refining.—Crude sulphur is generally contaminated with earthy impurities, from which it is separated by distillation. The operation is conducted as shown in Fig. 39. The crude sulphur is first introduced into the iron pot *A*, where it is melted. The greater part of the impurities sink to the bottom, and the melted sulphur is run off into the retort *B*, whence it is distilled into the large brick-work chamber *C*. When the distillation is conducted rapidly, so as to keep the temperature of the chamber above the melting-point of sulphur, the latter condenses in the liquid state and collects on the floor of the chamber, whence it may be drawn off by the tap *D*, to be run into slightly conical box-wood moulds. The sulphur thus obtained is known as *roll sulphur*. When the distillation proceeds slowly, and the temperature of the chamber is consequently lower, the sulphur is deposited as a fine crystal-

line dust on the walls and floor of the chamber. This form is termed *flowers of sulphur.*

FIG. 39.



Properties.—Sulphur is capable of existing in several allotropic modifications, of which the following are the most important:

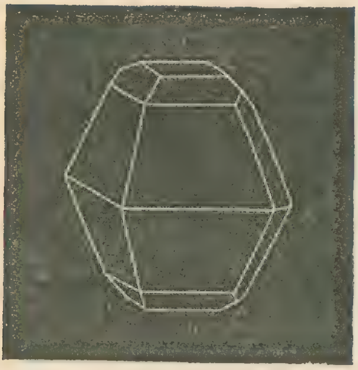
	Condition.	Specific gravity.	Behavior with carbonic disulphide.
α.	Rhombic (octahedral), . .	2.05	Soluble.
β.	Monoclinic (prismatic), . .	1.98	Transformed into *α*.
γ.	Plastic, ...	1.95	Insoluble.
δ.	Powder, ...	1.95	Insoluble.

The rhombic form is that in which sulphur occurs in nature. This form displays great variety of crystalline combinations: the most frequently occurring combination, in which the rhombic octahedron is dominant, is shown in Fig. 40. Rhombic sulphur is insoluble in water, somewhat soluble in alcohol, ether, and hydrocarbons, readily soluble in carbonic disulphide and disulphur dichloride. From these solvents it is again deposited in the rhombic form. Rhombic sulphur fuses at 114.5° C. (238.1° F.).

The behavior of melted sulphur is anomalous. Just above its fusing-point it forms a clear, yellow, mobile liquid; but on raising the temperature the color deepens, changing to a reddish-brown, whilst the liquid becomes viscid. At about 230° C. (446° F.) it is almost black,

and is so thick that the vessel in which it is contained may be inverted without spilling the contents. Heated above this temperature it again becomes liquid, still however preserving its dark color, till at 447° C. (836° F.) it boils, giving off a reddish-brown vapor. One litre of this vapor at 524° C. (975° F.) weighs 96 criths, whereas above 860° C. (1580° F.) the weight of 1 litre of sulphur vapor is 32 criths, or only

FIG. 40.

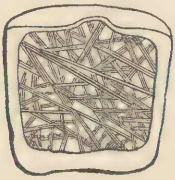


one-third of the first-mentioned value. From this it follows that above 860° C. the molecule of sulphur contains two atoms, but that just above its boiling-point, the molecule is hexatomic.

If sulphur, heated to its boiling-point, be allowed to cool gradually, the above changes are observed in the reverse order.

The rhombic variety of sulphur may also be obtained by melting sulphur in large masses, and, by slow cooling with exclusion of air, allowing it to remain in a state of superfusion, or suspended solidification.

FIG. 41.



At a temperature of about 90° C. (194° F.), the superfused sulphur deposits rhombic crystals. If the melted sulphur be allowed to cool more rapidly, the second or *monoclinic* variety is obtained. This last experiment is best performed by fusing about a kilogram of sulphur in a Hessian crucible, and allowing it to cool till a crust has been formed over the surface. Two holes are then broken in this crust, and the crucible is inclined so as to allow the sulphur which still remains liquid to run out. The interior of the crucible (Fig. 41) is found to be lined with long thin transparent prisms, belonging to the monoclinic system. These fuse at 120° C. (248° F.).

The system in which sulphur crystallizes is determined by the con-

ditions of temperature under which the crystallization occurs, and the crystals of each system are unstable at the temperature of formation of those of the other system. Thus, when a transparent crystal of rhombic sulphur, which has been deposited at ordinary temperatures, is exposed for some time to a temperature just below its fusing-point, it loses its transparency and, on examination, is found to have been converted into an aggregation of minute monoclinic crystals. On the other hand, the transparent crystals of monoclinic sulphur, which are formed at a higher temperature, become opaque after remaining for some time at the ordinary temperature, having changed into aggregations of small rhombic crystals. This latter change may also be effected by scratching the monoclinic crystals: in this case the transformation takes place rapidly, and is found to be accompanied by a liberation of heat. The rhombic modification is that into which all other forms of sulphur (except the δ variety) spontaneously change at ordinary temperatures.

If melted sulphur at a temperature just above its fusing-point be poured into cold water, it solidifies to a yellow, brittle mass. But if the temperature of the melted sulphur be raised above the point of maximum viscosity, and the dark-colored mobile liquid thus obtained be poured in a thin stream into water so as to effect its cooling as rapidly as possible, a totally different phenomenon is observed. Under these conditions, the sulphur forms plastic, amber-colored, transparent threads, which may be drawn out or kneaded between the fingers. This is the variety known as *plastic sulphur*. After standing for some time at ordinary temperatures it becomes brittle and opaque. At a temperature of 100° it is suddenly converted into rhombic sulphur, the change being accompanied by evolution of heat.

If the brittle sulphur resulting from the spontaneous change of the plastic variety be treated with carbonic disulphide, part of it is dissolved, whilst part remains behind as a brown amorphous powder. A light yellow amorphous powder, insoluble in carbonic disulphide, is also obtained by treating flowers of sulphur with this solvent as long as anything is dissolved. The same insoluble variety separates out when a solution of sulphur in carbon disulphide is exposed to sunlight concentrated by means of a lens. At a temperature of 100° C., these amorphous varieties pass into the ordinary rhombic modification.

All the varieties of sulphur are insoluble in water.

The so-called *milk of sulphur* is nothing more than sulphur in a finely divided state, obtained by decomposing calcic pentasulphide, or any other polysulphide, with hydrochloric acid:

$$\underset{\text{Calcic pentasulphide.}}{{}^{\text{viii}}(\mathbf{S}_5)''\text{Ca}} + \underset{\text{Hydrochloric acid.}}{2\text{HCl}} = \underset{\text{Calcic chloride.}}{\mathbf{Ca}\text{Cl}_2} + \underset{\text{Sulphuretted hydrogen.}}{\mathbf{S}\text{H}_2} + 4\text{S}.$$

It is soluble in carbonic disulphide, and is probably the rhombic variety.

Reactions—1. When heated in air or oxygen to its temperature of ignition, sulphur burns with a blue flame, forming sulphurous anhydride:

$$S + O_2 = \mathbf{SO_2}.$$
Sulphurous anhydride.

A slow, phosphorescent combustion occurs when sulphur is heated to about 180° C. (356° F.) in air. No flame is visible in daylight; but in the dark a grayish-white flame, quite distinct from the ordinary blue flame of burning sulphur, appears to hover over the heated surface. The product of combustion is in this case also sulphurous anhydride.

In presence of air and moisture, finely divided sulphur is spontaneously oxidized at ordinary temperatures to sulphurous and sulphuric acids.

2. Sulphur also unites directly with chlorine, bromine, iodine, phosphorus, hydrogen, and various other non-metals.

3. It combines directly with many metals when heated with them, forming sulphides:

$$K_2 + S = \mathbf{SK_2}.$$
Potassic sulphide.

$$Fe + S = \mathbf{FeS}.$$
Ferrous sulphide.

When united exclusively with positive elements or radicals, sulphur is almost invariably a dyad; it is then analogous to oxygen, as will be seen from the following formulæ:

Oxygen compounds, . .	$\mathbf{OK_2}$,	$\mathbf{OKH}$,	$\mathbf{CO_2}$,	$\mathbf{COKo_2}$.
Sulphur " . . .	$\mathbf{SK_2}$,	$\mathbf{SKH}$,	$\mathbf{CS''_2}$,	$\mathbf{CSKs_2}$.

Uses.—Sulphur is employed in the arts in the manufacture of gunpowder and for tipping common lucifer matches. In the form of sulphurous anhydride it is a useful bleaching agent. Its most important application, however, is in the manufacture of sulphuric acid.

COMPOUNDS OF SULPHUR WITH HYDROGEN.

Sulphuretted hydrogen, ...	$\mathbf{SH_2}$.
Hydrosulphyl, ...	$\mathbf{'S'_2H_2}$ or Hs_2.
Hyposulphurous hydrosulphate, . . .	$\mathbf{S}Hs_2$.

SULPHURETTED HYDROGEN, *Hydrosulphuric Acid, Sulphydric Acid.*

$$\mathbf{SH_2}.\quad H—S—H.$$

Molecular weight = 34. *Molecular volume* $\square\square$. 1 *litre weighs* 17 *criths. Solid at* —85.5° C. (—121.9° F.). *Liquefied under a pressure of* 17 *atmospheres at* 10° C. (50° F.).

History.—This compound was first investigated by Scheele.

Occurrence.—Sulphuretted hydrogen is evolved along with other gases from volcanoes and fumaroles. It occurs also in hepatic mineral

waters, such as those of Harrogate, and in waters which contain sulphates along with organic matters.

Formation and Preparation.—1. Sulphuretted hydrogen is formed in small quantity by the direct union of its elements when hydrogen, together with the vapor of sulphur, is passed through a red-hot tube, or even when hydrogen is passed into boiling sulphur:

$$H_2 + S = \underset{\text{Sulphuretted hydrogen.}}{\mathbf{SH_2}}.$$

2. The most convenient method of preparing the gas for laboratory purposes consists in acting on ferrous sulphide with dilute sulphuric acid:

$$\underset{\substack{\text{Ferrous}\\ \text{sulphide.}}}{\mathbf{FeS''}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{\mathbf{SO_2Ho_2}} = \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{\mathbf{SH_2}} + \underset{\substack{\text{Ferrous}\\ \text{sulphate.}}}{\mathbf{SO_2Feo''}}.$$

The ferrous sulphide, broken into coarse fragments, is introduced into a flask similar to that used in the preparation of hydrogen, and the acid, diluted with about 6 times its bulk of water, is poured in through a funnel. The gas is washed by passing it through water.

Hydrochloric acid may be substituted for sulphuric acid in the above reaction:

$$\underset{\substack{\text{Ferrous}\\ \text{sulphide.}}}{\mathbf{FeS''}} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl} = \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{\mathbf{SH_2}} + \underset{\substack{\text{Ferrous}\\ \text{chloride.}}}{\mathbf{FeCl_2}}.$$

The use of sulphuric acid is, however, much more convenient in practice.

3. Sulphuretted hydrogen prepared from ferrous sulphide generally contains free hydrogen, generated by the action of the acid upon metallic iron, which is often present in the sulphide as an impurity. Pure sulphuretted hydrogen may be obtained by decomposing precipitated antimonious sulphide, or native antimonious sulphide (*gray antimony ore*), with hydrochloric acid aided by a gentle heat:

$$\underset{\substack{\text{Antimonious}\\ \text{sulphide.}}}{\mathbf{Sb_2S''_3}} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{6HCl} = \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{3\mathbf{SH_2}} + \underset{\substack{\text{Antimonious}\\ \text{chloride.}}}{2\mathbf{SbCl_3}}.$$

If the native compound be employed, it ought to be first treated with dilute hydrochloric acid, in order to remove any carbonates that may be present.

4. Sulphuretted hydrogen is formed in small quantity along with sulphurous anhydride when steam is passed over boiling sulphur, or even when sulphur is boiled with water:

$$3S + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{2\mathbf{SH_2}} + \underset{\substack{\text{Sulphurous}\\ \text{anhydride.}}}{SO_2}.$$

The sulphuretted hydrogen and sulphurous anhydride mutually decompose each other in the distillate with separation of sulphur, only a portion of the former gas remaining (see p. 243).

5. Sulphuretted hydrogen is formed when sulphur is heated along with paraffin, aniline, and various other organic bodies. The reactions which take place in these cases are very complicated and cannot be followed by means of equations.

6. It is evolved during the putrefaction of organic bodies containing sulphur, and also when these bodies are subjected to destructive distillation. It thus finds its way into illuminating gas, from which it has to be removed in the process of purification.

Properties.—Sulphuretted hydrogen is a colorless gas possessing the disgusting odor of putrid eggs. The very offensive odor of the gas prepared from ferrous sulphide is, however, in part due to the presence of volatile sulpho-carbon compounds derived from the iron. It is slightly heavier than air. It is combustible, burning in air or oxygen with a bluish flame, and forming sulphurous anhydride and water:

$$\underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2} + 3O = \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{SO_2} + \underset{\text{Water.}}{OH_2}.$$

When the supply of oxygen is insufficient for complete combustion, water only is formed, and sulphur is deposited.

Water absorbs about three times its volume of sulphuretted hydrogen, yielding a colorless solution possessing the taste and odor of the gas. The aqueous solution is a useful laboratory reagent. It parts with the whole of its gas on boiling. Exposed to the air, the gas in solution is quickly oxidized with separation of sulphur, water being formed at the same time.

Sulphuretted hydrogen has a powerfully poisonous action when inhaled, especially in the case of small animals. The intensity of the action in various animals appears to be connected with the rapidity of circulation of the blood. An atmosphere containing $\frac{1}{1500}$ of the gas suffices to kill a bird, whilst $\frac{1}{800}$ is necessary to kill a dog, and $\frac{1}{200}$ to kill a horse. Cold-blooded animals are totally unaffected by this proportion of sulphuretted hydrogen.

Reactions.—1. Sulphuretted hydrogen is immediately decomposed by chlorine with separation of sulphur:

$$\underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2} + Cl_2 = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} + S.$$

A similar reaction takes place with bromine. In the case of iodine, the formation of hydriodic acid and the liberation of sulphur take place only in the presence of water. The reason of this is that the reaction

$$\underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2} + I_2 = \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{2HI} + S,$$

is attended with an absorption of heat, and consequently, according to the laws of thermochemistry (p. 115), cannot take place without the

aid of some extraneous energy. When water is present, the heat evolved by the absorption of the hydriodic acid by water, furnishes this energy; the thermal sign of the equation becomes positive and the reaction possible.

2. Sulphuretted hydrogen is decomposed by many compounds rich in oxygen, such as ferric hydrate:

$$\underset{\substack{\text{Ferric}\\\text{hydrate.}}}{Fe'''_2Ho_6} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3SH_2} = \underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{2FeS''} + S + \underset{\text{Water.}}{6OH_2}.$$

This reaction is employed on a large scale in the purification of coal-gas (see p. 245).

In like manner it reduces concentrated sulphuric acid, which cannot therefore be employed in drying the gas:

$$\underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{SO_2Ho_2} = \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{SO_2} + S + \underset{\text{Water.}}{2OH_2}.$$

Fuming nitric acid, when dropped into a jar of sulphuretted hydrogen, oxidizes it with explosive violence.

3. The sulphydrates and sulphides of the metals are produced by the action of sulphuretted hydrogen on the hydrates and oxides; thus:

$$\underset{\substack{\text{Potassic}\\\text{hydrate.}}}{OKH} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2} = \underset{\substack{\text{Potassic}\\\text{sulphydrate.}}}{SKH} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\substack{\text{Baric}\\\text{hydrate.}}}{BaHo_2} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{2SH_2} = \underset{\substack{\text{Baric}\\\text{sulphydrate.}}}{BaHs_2} + \underset{\text{Water.}}{2OH_2}.$$

$$\underset{\substack{\text{Argentic}\\\text{oxide.}}}{OAg_2} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2} = \underset{\substack{\text{Argentic}\\\text{sulphide.}}}{SAg_2} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\substack{\text{Cupric}\\\text{oxide.}}}{CuO} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2} = \underset{\substack{\text{Cupric}\\\text{sulphide.}}}{CuS} + \underset{\text{Water.}}{OH_2}.$$

Upon this property, and upon the varying behavior of the different metallic sulphides towards weak acids, is based the use of sulphuretted hydrogen as a reagent in analysis. Some of these sulphides are insoluble in weak acids: sulphuretted hydrogen, therefore, precipitates them from an acid solution of the salts of their metals:

$$\underset{\substack{\text{Cupric}\\\text{sulphate.}}}{SO_2Cuo''} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{SH_2} = \underset{\substack{\text{Cupric}\\\text{sulphide.}}}{CuS} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{SO_2Ho_2}.$$

Others are soluble in weak acids, but insoluble in alkaline solutions. The precipitation of these sulphides is most conveniently effected by the

addition of an alkaline sulphide (ammonic sulphide is most commonly employed for this purpose) to the neutral or alkaline solution of the salt, when double decomposition takes place, thus:

$$\underset{\text{Zincic chloride.}}{\mathbf{Zn}Cl_2} + \underset{\text{Ammonic sulphide.}}{\mathbf{S}(NH_4)_2} = \underset{\text{Zincic sulphide.}}{\mathbf{ZnS}} + \underset{\text{Ammonic chloride.}}{2\mathbf{N}H_4Cl}.$$

A third class of metals yields sulphides which are soluble in water, and are therefore not precipitated either in acid or in alkaline solutions. It is thus possible to divide the metals into three groups, according to the behavior of their sulphides, and this division forms one of the foundations of inorganic qualitative analysis.

4. Most metals when heated in sulphuretted hydrogen combine with the sulphur to form sulphides, whilst hydrogen is liberated:

$$Sn + \underset{\text{Sulphuretted hydrogen.}}{\mathbf{S}H_2} = \underset{\text{Stannous sulphide.}}{\mathbf{Sn}''S} + H_2.$$

Silver becomes tarnished when exposed at ordinary temperatures to the action of sulphuretted hydrogen in presence of air, owing to the formation of a superficial coating of argentic sulphide (*q. v.*), but the action is very slow unless moisture be present.

Composition.—The composition of sulphuretted hydrogen is best ascertained by heating in it some metal which combines with the sulphur liberating the hydrogen. Tin is usually employed for this purpose (see above). (Potassium or sodium cannot be used, as in these cases the metal displaces only one-half of the hydrogen, combining with a semi-molecule of hydrosulphyl to form a sulphydrate.) The operation is performed in a bent tube over mercury as described in the analysis of hydrochloric acid (p. 159). After the action is complete and the tube has been allowed to cool, it will be found that the hydrogen occupies exactly the same volume as the sulphuretted hydrogen employed. Sulphuretted hydrogen thus contains its own volume of hydrogen. Therefore:

Weight of 1 litre of sulphuretted hydrogen,	17 criths.
Deduct weight of 1 litre of hydrogen, . .	1 crith.
There remain	16 criths.

which is the weight of half a litre of normal sulphur vapor. Calculating to whole volumes, 2 volumes of hydrogen combine with 1 volume of sulphur vapor to form 2 volumes of sulphuretted hydrogen. By weight, the proportion of hydrogen to sulphur is as 1 : 16 or as 2 : 32, and the formula of the compound is therefore $\mathbf{S}H_2$.

HYDROSULPHYL, *Hydric Persulphide.*

$'\mathbf{S}'_2H_2$ or Hs_2.
H—S—S—H.

Probable molecular weight = 66. *Sp. gr.* 1.769.

Preparation.—When a solution of calcic disulphide is poured into an excess of cold concentrated hydrochloric acid, hydrosulphyl separates out as a heavy yellowish oil:

$$\underset{\text{Calcic disulphide.}}{'\mathbf{S}'_2Ca''} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Hydrosulphyl.}}{'\mathbf{S}'_2H_2} + \underset{\text{Calcic chloride.}}{\mathbf{Ca}Cl_2}.$$

The calcic disulphide is prepared by boiling milk of lime with an excess of sulphur and filtering. The solution must be poured into the acid, and not the reverse, as hydrosulphyl is much more stable in contact with acids than in contact with alkalies. The calcic disulphide prepared as above, is always mixed with higher polysulphides, but these also yield hydrosulphyl, mixed however with sulphur.

Properties.—Hydrosulphyl is a heavy yellowish liquid possessing a fetid odor. It closely resembles hydroxyl in its properties, bleaching organic coloring matters and reducing argentic oxide. It is very unstable, and is gradually decomposed into sulphuretted hydrogen and free sulphur. Owing to this fact and to the property which hydrosulphyl possesses of dissolving sulphur, it has been found almost impossible to obtain it in a state of purity, and its composition is more a matter of conjecture, based upon its analogy with hydroxyl, than a strict analytical result.

HYPOSULPHUROUS HYDROSULPHATE.

$$\mathbf{S}Hs_2, \text{ or } \left\{\begin{array}{l} Hs \\ S''. \\ Hs \end{array}\right.$$

Probable molecular weight = 98.

Preparation.—When a cold saturated solution of strychnine in alcohol is mixed with an alcoholic solution of yellow ammonic sulphide, a compound is formed crystallizing in orange needles of the formula $B_{21}H_{22}N_2O_2,H_2S_3$. By the action of concentrated sulphuric acid upon this compound, and subsequent dilution with water, hyposulphurous hydrosulphate is liberated as a yellow oily body. It closely resembles in its properties hydrosulphyl, and, like that substance, undergoes spontaneous decomposition into sulphuretted hydrogen and sulphur.

COMPOUNDS OF SULPHUR WITH THE HALOGENS.

Disulphur dichloride, ...	$'\mathbf{S}'_2Cl_2$.
Hyposulphurous chloride, ...	$\mathbf{S}Cl_2$.
Sulphurous chloride, ...	$\mathbf{S}Cl_4$.
Disulphur dibromide, ...	$'\mathbf{S}'_2Br_2$.
Disulphur diniodide, ...	$'\mathbf{S}'_2I_2$.
Sulphuric iodide, ...	$\mathbf{S}I_6$.

DISULPHUR DICHLORIDE.

$'\mathbf{S}'_2Cl_2$.

Molecular weight = 135. *Molecular volume* $\square\square$. 1 *litre of disulphur dichloride vapor weighs* 67.5 *criths. Specific gravity of liquid* 168. *Boils at* 139° C. (282.2° F.).

Preparation.—A current of thoroughly dried chlorine is passed over the surface of heated sulphur contained in a retort. The disulphur dichloride distils over as fast as it is formed and collects in the cooled receiver. The process must be interrupted before all the sulphur is converted into the chloride, and the product must be purified by rectification.

$$S_2 + Cl_2 = \underset{\text{Disulphur dichloride.}}{'\mathbf{S}'_2Cl_2}.$$

Properties.—Disulphur dichloride is an amber-colored, fuming liquid, possessing a disagreeable pungent odor. Its vapor irritates the eyes. It dissolves sulphur freely, a property which is utilized in the manufacture of vulcanized india-rubber.

Reaction.—In contact with water it is gradually decomposed with formation of hydrochloric acid and sulphurous anhydride, whilst sulphur is deposited:

$$\underset{\substack{\text{Disulphur}\\\text{dichloride.}}}{2'\mathbf{S}'_2Cl_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl} + \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{\mathbf{S}O_2} + 3S.$$

HYPOSULPHUROUS CHLORIDE.

$\mathbf{S}Cl_2$.

This compound is prepared by saturating disulphur dichloride with chlorine at 0°. On removing the excess of chlorine by a stream of dry carbonic anhydride, the hyposulphurous chloride remains behind as a dark-red liquid. It is very unstable, spontaneously decomposing at ordinary temperatures into disulphur dichloride and chlorine. On attempting to distil it, this decomposition takes place rapidly. With water it is decomposed like disulphur dichloride.

SULPHUROUS CHLORIDE.

$\mathbf{S}Cl_4$.

Sulphurous chloride is obtained as a yellowish-brown, very mobile liquid by saturating disulphur dichloride with chlorine at a temperature of from —20° to —22° C. (—4° to —8° F.). It is even less stable than the foregoing compound, and can exist only at temperatures below —20° C. (—4° F.). When removed from the freezing mixture it rapidly evolves chlorine, and is converted into hyposulphurous chloride. Water decomposes it with violence, forming sulphurous anhydride and hydrochloric acid:

$$\underset{\substack{\text{Sulphurous}\\\text{chloride.}}}{\mathbf{S}Cl_4} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{\mathbf{S}O_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl}.$$

DISULPHUR DIBROMIDE.

$'S'_2Br_2$.

This compound is formed by the direct union of its elements. It forms a heavy red liquid which distils with partial decomposition between 210° and 220° C.

DISULPHUR DINIODIDE.

$'S'_2I_2$.

Disulphur diniodide is obtained as a dark-gray crystalline mass by heating sulphur and iodine together under water.

SULPHURIC IODIDE.

SI_6.

This substance is obtained in crystals when a solution of iodine and sulphur in carbonic disulphide is allowed to evaporate. It is interesting as a compound of hexadic sulphur in which all the six bonds are satisfied by monads.

COMPOUND OF SULPHUR WITH CARBON.

CARBONIC DISULPHIDE, *Bisulphide of Carbon.*

CS_2.

Molecular weight = 76. *Molecular volume* ☐☐. 1 *litre of carbonic disulphide vapor weighs* 38 *criths. Sp. gr. of liquid* 1.293. *Fuses at* —100° C. (—180° F.). *Boils at* 46.6° C. (115.9° F.).

History.—Carbonic disulphide was discovered by Lampadius in 1796.

Preparation.—1. This compound is formed by the direct combination of its elements at a high temperature. A tubulated earthenware retort, filled with pieces of charcoal and furnished with a vertical porcelain tube luted to the tubulure and passing to the bottom of the retort, is heated to redness. Fragments of sulphur are introduced one at a time through the porcelain tube, the latter being closed at the top after each addition. The sulphur volatilizes and its vapor combines with the carbon forming carbonic disulphide, which distils over and is condensed as a liquid and collected under water:

$$C + S_2 = \underset{\text{Carbonic disulphide.}}{CS_2}.$$

Sulphuretted hydrogen is formed at the same time owing to the combination of the sulphur with the hydrogen which is invariably present in charcoal. The crude product is redistilled in order to free it from dissolved sulphur. Thus prepared it possesses a peculiar, fetid odor, due to the presence of other volatile sulphur compounds. These may be

removed by shaking the liquid with mercury or corrosive sublimate, subjecting it afterwards to a further distillation.

2. It is also formed when charcoal is heated with iron- or copper-pyrites. This was the method employed by Lampadius. The reaction is due to the sulphur which is given off by the pyrites on heating, and is essentially the same as the foregoing:

$$\underset{}{C} + \underset{\substack{\text{Iron-pyrites}\\\text{(Ferric disulphide).}}}{2FeS_2} = \underset{\substack{\text{Carbonic}\\\text{disulphide.}}}{CS''_2} + \underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{2FeS''}.$$

It is to the occurrence of iron-pyrites in coal that the presence of carbonic disulphide vapor in coal-gas is due. This impurity, on account of the difficulties attending its removal, has long been the source of annoyance both to the gas manufacturer and the consumer.

Properties.—Carbonic disulphide is a colorless, powerfully refracting, mobile liquid. When pure, it possesses a sweetish, ethereal odor. It solidifies at — 116° C. (— 177° F.) and fuses at — 110° C. (— 166° F.). It dissolves sulphur, phosphorus, iodine, caoutchouc, oils, and fats. Sulphur and phosphorus may be obtained in crystals by the spontaneous evaporation of their solutions in carbonic disulphide. It is extensively employed in manufacturing processes as a solvent.

Carbonic disulphide is exceedingly inflammable. Its vapor inflames in the air at 149° C. (300° F.), and may be ignited by bringing a test tube of paraffin heated to this temperature in contact with it. It burns with a blue flame, yielding carbonic anhydride and sulphurous anhydride:

$$\underset{\substack{\text{Carbonic}\\\text{disulphide.}}}{CS''_2} + 3O_2 = \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2} + \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{2SO_2}.$$

A mixture of the vapor with air or oxygen explodes with great violence on the approach of a flame. Mixed with nitric oxide and inflamed, the vapor burns, emitting a brilliant blue light, very rich in rays of high refrangibility.

Carbonic disulphide is highly poisonous. Its vapor, inhaled in large quantities, proves speedily fatal, and even in minute quantity is very dangerous when habitually inhaled (as, for instance, in factories in which it is employed), owing to a specific action on the nervous system.

Reactions.—1. Heated potassium burns in the vapor of carbonic disulphide with formation of potassic sulphide and liberation of carbon:

$$\underset{\substack{\text{Carbonic}\\\text{disulphide.}}}{CS''_2} + 2K_2 = \underset{\substack{\text{Potassic}\\\text{sulphide.}}}{2SK_2} + C.$$

2. When brought into contact with a solution of an alkaline hydrate, carbonic disulphide is decomposed, a carbonate and a sulphocarbonate being formed:

$$\underset{\substack{\text{Potassic}\\\text{hydrate.}}}{6OKH} + \underset{\substack{\text{Carbonic}\\\text{disulphide.}}}{3CS''_2} = \underset{\substack{\text{Potassic}\\\text{sulphocarbonate.}}}{2CS''Ks_2} + \underset{\substack{\text{Potassic}\\\text{carbonate.}}}{COKo_2} + \underset{\text{Water.}}{3OH_2}.$$

3. In contact with solutions of alkaline sulphides, carbonic disulphide also forms alkaline sulphocarbonates:

$$SK_2 + CS''_2 = CS''Ks_2.$$

Potassic sulphide.	Carbonic disulphide.	Potassic sulphocarbonate.

4. When the vapor of carbonic disulphide is passed over heated calcic hydrate it is decomposed, carbonic anhydride and sulphuretted hydrogen being evolved:

$$CS_2 + 2CaHo_2 = 2CaO + CO_2 + 2SH_2.$$

This reaction has been successfully employed in removing carbonic disulphide from illuminating gas.

Carbonic disulphide is, as has already been pointed out, the sulphur compound corresponding to carbonic anhydride. A carbonic monosulphide, corresponding to carbonic oxide, has not been prepared.

SULPHOCARBONIC ACID.

$CS''Hs_2$.

Preparation.—This compound is obtained as a reddish-brown oily liquid by the action of hydrochloric acid on ammonic sulphocarbonate:

$$CS''(NH_4S)_2 + 2HCl = CS''Hs_2 + 2NH_4Cl.$$

Ammonic sulphocarbonate.	Hydrochloric acid.	Sulpho-carbonic acid.	Ammonic chloride.

COMPOUND OF SULPHUR WITH CARBON AND OXYGEN.

CARBONIC OXYSULPHIDE.

COS''.

Molecular weight = 60. *Molecular volume* ◻◻. 1 *litre of carbonic oxysulphide weighs* 30 *criths. Gaseous.*

History.—This gas, which in composition lies intermediate between carbonic anhydride and carbonic disulphide, was discovered by C. von Than.

Occurrence.—It appears to exist in solution in the waters of certain mineral springs.

Preparation.—1. Carbonic oxysulphide is formed when a mixture of carbonic oxide and sulphur vapor is passed through a heated tube:

$$CO + S = COS''.$$

Carbonic oxide.		Carbonic oxysulphide.

2. It is most readily obtained by the action of moderately strong sulphuric acid upon potassic sulphocyanide:

$$\begin{array}{ccccccc} \mathbf{C}NKs & + & 2\mathbf{S}O_2Ho_2 & + & \mathbf{O}H_2 & = & \mathbf{C}O\mathbf{S}'' \\ \text{Potassic sulphocyanide.} & & \text{Sulphuric acid.} & & \text{Water.} & & \text{Carbonic oxysulphide.} \end{array}$$

$$\begin{array}{cccc} + & \mathbf{S}O_2HoKo & + & \mathbf{S}O_2Ho(N^{v}H_4O). \\ & \text{Hydric potassic sulphate.} & & \text{Hydric ammonic sulphate.} \end{array}$$

By regulating the temperature a steady evolution of the gas is obtained.

Properties.—Carbonic oxysulphide is a colorless gas with a peculiar odor. It is readily inflammable, and forms with oxygen a mixture which explodes on the approach of a flame. It is soluble in its own volume of water, to which it imparts its characteristic odor.

Reactions.—1. A platinum wire heated to whiteness by means of the voltaic current decomposes the gas into sulphur and carbonic oxide, the latter occupying the same volume as the carbonic oxysulphide employed.

2. With caustic alkalies it yields a mixture of carbonate and sulphide:

$$\begin{array}{ccccccccc} \mathbf{C}O\mathbf{S}'' & + & 4KHo & = & \mathbf{C}OKo_2 & + & \mathbf{S}K_2 & + & 2\mathbf{O}H_2. \\ \text{Carbonic oxysulphide.} & & \text{Potassic hydrate.} & & \text{Potassic carbonate.} & & \text{Potassic sulphide.} & & \text{Water.} \end{array}$$

COMPOUNDS OF SULPHUR WITH OXYGEN AND HYDROXYL.

In these compounds the sulphur is either a dyad, a tetrad, or a hexad.

Sulphurous anhydride, $\mathbf{S}O_2$. $\quad O{=}S{=}O.$

Sulphurous acid, . . $\mathbf{S}OHo_2$.

$$\begin{array}{ccccccccc} & & & & O & & & & \\ & & & & \| & & & & \\ H & — & O & — & S & — & O & — & H. \end{array}$$

Sulphuric anhydride, . $\mathbf{S}O_3$.

$$\begin{array}{ccccc} & & O & & \\ & & \| & & \\ O & = & S & = & O. \end{array}$$

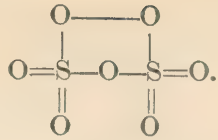
Sulphuric acid (*Hydric sulphate*), . . $\mathbf{S}O_2Ho_2$.

$$\begin{array}{ccccccccc} & & & & O & & & & \\ & & & & \| & & & & \\ H & — & O & — & S & — & O & — & H. \\ & & & & \| & & & & \\ & & & & O & & & & \end{array}$$

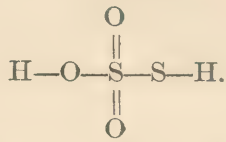
Pyrosulphuric acid (*Dihydric disulphate*), ... $\left\{\begin{array}{l} \mathbf{S}O_2Ho \\ O \\ \mathbf{S}_2OHo \end{array}\right.$.

$$\begin{array}{ccccccccccccc} & & & & O & & & & O & & & & \\ & & & & \| & & & & \| & & & & \\ H & — & O & — & S & — & O & — & S & — & O & — & H. \\ & & & & \| & & & & \| & & & & \\ & & & & O & & & & O & & & & \end{array}$$

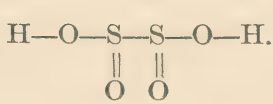
Persulphuric anhydride, $\left\{\begin{matrix} SO_2\text{—}O \\ O \\ SO_2\text{—}O \end{matrix}\right\}$



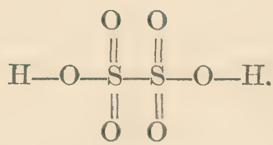
Thiosulphuric acid (*Hyposulphurous acid*), $\}$ SO_2HoHs.



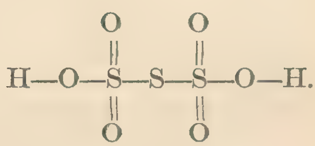
Dithionous acid (*Hydrosulphurous acid*), . . $\left\{\begin{matrix} SOHo \\ SOHo \end{matrix}\right.$.



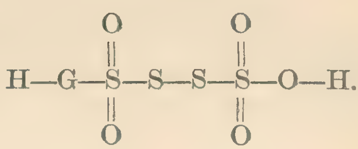
Dithionic acid, . . . $\left\{\begin{matrix} SO_2Ho \\ SO_2Ho \end{matrix}\right.$.



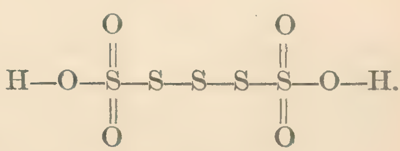
Trithionic acid (*Sulpho-dithionic acid*), . . . $\left\{\begin{matrix} SO_2Ho \\ S'' \\ SO_2Ho \end{matrix}\right.$.



Tetrathionic acid (*Di-sulpho-dithionic acid*), $\left\{\begin{matrix} SO_2Ho \\ S'' \\ S'' \\ SO_2Ho \end{matrix}\right.$.



Pentathionic acid (*Tri-sulpho-dithionic acid*), $\left\{\begin{matrix} SO_2Ho \\ S'' \\ S'' \\ S'' \\ SO_2Ho \end{matrix}\right.$



SULPHUROUS ANHYDRIDE.

SO_2.

Molecular weight = 64. *Molecular volume* □□. 1 *litre weighs* 32 *criths. Solid at* — 76° C. (—104.8° F.). *Liquid under a pressure of two atmospheres at* 7° C. (44.6° F.).

Occurrence.—This compound, which is gaseous at ordinary temperatures, occurs in nature as a volcanic product, either in the gases issu-

ing from volcanoes, or dissolved in volcanic springs. It is also found in small quantities in the air of towns, being derived in this case from the combustion of the pyrites contained in coal. It is evolved in the operation of roasting sulphureous ores.

Preparation.—1. When sulphur is burnt in air or oxygen, direct combination takes place according to the following equation:

$$\underset{}{S} + \underset{}{O_2} = \underset{\text{Sulphurous anhydride.}}{SO_2}.$$

This is the process employed when sulphurous anhydride is required on a large scale, as in the manufacture of sulphuric acid. In this case the combustion of pyrites is frequently substituted for that of sulphur.

2. It may also be prepared by heating a mixture of about three parts by weight of sulphur with four of manganic peroxide:

$$S_2 + \underset{\substack{\text{Manganic}\\ \text{peroxide.}}}{MnO_2} = \underset{\substack{\text{Sulphurous}\\ \text{anhydride.}}}{SO_2} + \underset{\substack{\text{Manganous}\\ \text{sulphide.}}}{MnS''}.$$

3. The foregoing processes consist in oxidizing sulphur. But it is also possible to start from a higher oxide of sulphur and, by depriving it of a portion of its oxygen, to descend to sulphurous anhydride. Thus, if concentrated sulphuric acid be heated with copper or mercury, an oxide of the metal is formed, which combines with the excess of acid to form a sulphate, and the sulphuric acid is reduced to sulphurous acid. This latter, being a very unstable compound, is decomposed into sulphurous anhydride and water. Thus:

$$\underset{\text{Sulphuric acid.}}{2SO_2Ho_2} + Cu = \underset{\substack{\text{Sulphurous}\\ \text{anhydride.}}}{SO_2} + \underset{\substack{\text{Cupric}\\ \text{sulphate.}}}{SO_2Cuo''} + \underset{\text{Water.}}{2OH_2}.$$

$$\underset{\text{Sulphuric acid.}}{2SO_2Ho_2} + Hg = \underset{\substack{\text{Sulphurous}\\ \text{anhydride.}}}{SO_2} + \underset{\substack{\text{Mercuric}\\ \text{sulphate.}}}{SO_2Hgo''} + \underset{\text{Water.}}{2OH_2}.$$

It is necessary for the purpose to employ metals which do not evolve hydrogen with sulphuric acid, otherwise the sulphurous anhydride would be contaminated with this gas. The method with copper is that generally resorted to for laboratory purposes. The copper in the form of turnings or clippings is introduced into a capacious flask fitted with safety and delivery tubes. The acid is poured on the copper, and heat is applied to start the reaction. The heat must then be moderated, otherwise the mixture is apt to froth over.

4. Charcoal may be substituted for copper in the foregoing reaction, but in this case the sulphurous anhydride will be mixed with half its volume of carbonic anhydride.

$$\underset{\text{Sulphuric acid.}}{2SO_2Ho_2} + C = \underset{\substack{\text{Sulphurous}\\ \text{anhydride.}}}{2SO_2} + \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{CO_2} + \underset{\text{Water.}}{2OH_2}.$$

For the purposes for which sulphurous anhydride is usually required in the laboratory—*e.g.*, in the preparation of the alkaline sulphites or of an aqueous solution of the gas—the presence of carbonic anhydride is not objectionable. Sulphurous anhydride in excess expels carbonic anhydride from the alkaline carbonates, and the latter gas is nearly insoluble in water saturated with sulphurous anhydride.

5. If sulphur be heated with concentrated sulphuric acid, the two processes of oxidation of the sulphur and reduction of the sulphuric acid occur simultaneously, and sulphurous anhydride is obtained from both sources:

$$\underset{\text{Sulphuric acid.}}{2SO_2Ho_2} + S = \underset{\text{Sulphurous anhydride.}}{3SO_2} + \underset{\text{Water.}}{2OH_2}.$$

Properties.—Sulphurous anhydride is a colorless gas possessing the suffocating odor of burning sulphur. Its specific gravity is 2.211 (air = 1). It reddens a solution of litmus and afterwards bleaches it.

Sulphurous anhydride may be liquefied at ordinary pressures by the aid of cold. The apparatus employed for this purpose consists of a glass worm surrounded by a mixture of ice and salt. The lower opening of the worm passes through the neck of a small strong flask, which is also surrounded by a freezing-mixture. The neck of the flask, which has been previously contracted at one point, must be sealed with the blowpipe when a sufficient quantity of the liquid has been collected.

Another method of obtaining liquid sulphurous anhydride consists in sealing into a thick glass tube a mixture of one part of sulphur with five parts of sulphuric anhydride. The following reaction occurs:

$$S + \underset{\text{Sulphuric anhydride.}}{2SO_3} = \underset{\text{Sulphurous anhydride.}}{3SO_2}.$$

The change takes place spontaneously. The contents of the tube assume a blue color which in the course of a few days disappears, the two solid substances having been transformed into a colorless liquid.

Liquid sulphurous anhydride may be employed to produce intense cold by its evaporation. When evaporated rapidly *in vacuo*, the temperature of the sulphurous anhydride sinks to — 76° C. (— 104.8° F.), at which point the liquid solidifies to a white mass.

Reactions.—1. Water readily absorbs sulphurous anhydride, forming a solution of sulphurous acid. On cooling to 0° C. cubical crystals of the formula $SOHo_2,14OH_2$ are deposited:

$$\underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Water.}}{OH_2} = \underset{\text{Sulphurous acid.}}{SOHo_2}.$$

Water at 0° C. dissolves 80 times its volume of sulphurous anhydride, and 39 times its volume at 20° C. (68° F.). The solubility decreases rapidly as the temperature rises, and by boiling the liquid, the whole of the gas is expelled.

2. Sulphurous anhydride when passed into solutions of the metallic hydrates produces sulphites. If the sulphurous anhydride be in excess, an acid sulphite is obtained:

$$\underset{\text{Potassic hydrate.}}{OKH} + \underset{\text{Sulphurous anhydride.}}{SO_2} = \underset{\text{Hydric potassic sulphite.}}{SOHoKo.}$$

If the metallic hydrate be in excess the normal sulphite is formed, thus:

$$\underset{\text{Potassic hydrate.}}{2OKH} + \underset{\text{Sulphurous anhydride.}}{SO_2} = \underset{\text{Normal potassic sulphite.}}{SOKo_2} + \underset{\text{Water.}}{OH_2}.$$

Sulphurous acid, when acted upon by metallic hydrates, produces the same salts:

$$OKH + SOHo_2 = SOHoKo + OH_2;$$
$$2OKH + SOHo_2 = SOKo_2 + 2OH_2.$$

The sulphites, with the exception of those of the alkalies, are difficult of solution in water.

3. Sulphurous anhydride, when passed over metallic peroxides, unites directly with them to form sulphates.

$$\underset{\text{Plumbic peroxide.}}{PbO_2} + \underset{\text{Sulphurous anhydride.}}{SO_2} = \underset{\text{Plumbic sulphate.}}{SO_2Pbo''.}$$

The plumbic peroxide glows spontaneously when introduced into the gas.

4. In presence of substances which readily unite with hydrogen, sulphurous anhydride decomposes water, forming sulphuric acid and liberating hydrogen. It thus acts as a powerful reducing agent:

$$\underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + H_2.$$

It is upon this property that its bleaching powers depend. Vegetable colors exposed to the action of a solution of sulphurous acid are transformed into colorless compounds. The coloring matters are not destroyed, as is the case in bleaching with chlorine, and may be restored to their original condition by exposure to the air. It is therefore necessary to wash the bleached fabric thoroughly with pure water in order to prevent the color from returning. It is probable that in many cases the sulphurous acid enters directly into combination with the coloring matter to form a colorless compound, as the color may frequently be restored by treatment with weak alkaline or acid solutions. Sulphurous acid is employed in bleaching wool and silk, on which chlorine would act injuriously. The yellow color which new flannel assumes when first washed with soap is an instance of the action of

alkalies in restoring a color which has been discharged by sulphurous acid.

5. Sulphurous anhydride, in presence of water, converts iodine into hydriodic acid:

$$\underset{}{I_2} + \underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Hydriodic acid.}}{2HI} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2}.$$

On the other hand, sulphuric acid and hydriodic acid mutually decompose each other according to the equation:

$$\underset{\text{Hydriodic acid.}}{2HI} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = I_2 + \underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Water.}}{2OH_2}.$$

This reaction is the reverse of that first mentioned. The relative affinities of the substances here entering into chemical action vary with the concentration, and the predominance of the one or the other of these two reactions depends upon the proportion of sulphurous anhydride present in solution. Bunsen has shown that when the solution does not contain more than 0.05 per cent. of sulphurous anhydride, the influence of the second of the above reactions disappears, and the reduction of iodine to hydriodic acid is complete. Beyond this degree of concentration the second reaction comes into play, and the reduction is only partial. Bunsen has founded upon these observations a method for the quantitative determination of iodine, and indirectly of a vast number of oxidizable or reducible substances (Bunsen, *Ann. Chem. Pharm.*, **86**, 265, or Watts, *Dictionary of Chem.*, First Ed., **1**, 265).

6. At a temperature of 1200° C. (2192° F.) sulphurous anhydride is decomposed into sulphur and oxygen, part of the oxygen combining with the undecomposed sulphurous anhydride to form sulphuric anhydride. Tyndall has shown that sulphurous anhydride undergoes a similar decomposition when a beam of sunlight is passed through a long tube filled with this gas. A white mist, consisting of finely divided sulphur and sulphuric anhydride, appears in the tube:

$$\underset{\text{Sulphurous anhydride.}}{3SO_2} = \underset{\text{Sulphuric anhydride.}}{2SO_3} + S.$$

Detection.—Sulphites are recognized by the suffocating odor of sulphurous anhydride which they evolve on the addition of a strong acid, such as sulphuric acid:

$$\underset{\text{Potassic sulphite.}}{SOKo_2} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Potassic sulphate.}}{SO_2Ko_2} + \underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Water.}}{OH_2}.$$

When solutions of sulphites are mixed with a solution of argentic nitrate, a white precipitate of argentic sulphide is formed:

$$\underset{\substack{\text{Potassic}\\ \text{sulphite.}}}{SOKo_2} + \underset{\substack{\text{Argentic}\\ \text{nitrate.}}}{2NO_2Ago} = \underset{\substack{\text{Argentic}\\ \text{sulphite.}}}{SOAgo_2} + \underset{\substack{\text{Potassic}\\ \text{nitrate.}}}{2NO_2Ko}.$$

When this argentic sulphite is boiled with water, it becomes black, owing to the separation of metallic silver:

$$\underset{\substack{\text{Argentic}\\ \text{sulphite.}}}{SOAgo_2} + \underset{\text{Water.}}{OH_2} = \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{SO_2Ho_2} + Ag_2.$$

When a strip of paper moistened with potassic iodate and starch is exposed to the action of sulphurous anhydride, it assumes a magnificent blue color, owing to the reduction of the iodic acid to iodine, and the formation of iodide of starch. This is a very delicate test for traces of sulphurous anhydride.

Composition.—The composition of sulphurous anhydride may be readily determined by synthesis. A piece of sulphur is introduced into a flask of oxygen inverted over mercury, and the height of the mercury in the neck of the flask is carefully noted. The sulphur is then inflamed by means of a platinum wire rendered incandescent by the electric current. The sulphur burns in the oxygen, forming sulphurous anhydride. When the combustion is complete, the apparatus is allowed to cool, and the height of the mercury is again noted. It will be found that the volume of gas is the same as before. Sulphurous anhydride therefore contains its own volume of oxygen. Supposing 2 litres of oxygen to have been taken, and 2 litres of sulphurous anhydride to have been formed:

Weight of 2 litres of sulphurous anhydride,	64 criths.
Deduct weight of 2 litres of oxygen, . . .	32 criths.
There remain	32 criths.

which is the weight of 1 litre of normal sulphur vapor. Therefore 1 volume of sulphur vapor has combined with 2 volumes of oxygen to form 2 volumes of sulphurous anhydride. By weight: sulphurous anhydride contains 32 parts of sulphur combined with 32 (or 2×16) parts of oxygen, and its formula is therefore SO_2.

SULPHURIC ANHYDRIDE.

SO_3.

Molecular weight = 80. *Molecular volume* □□. 1 *litre of sulphuric anhydride vapor weighs* 40 *criths. Fuses at* 16° C. (60.8° F.). *Boils at* 46° C. (114.8° F.).

Preparation.—1. When a mixture of two volumes of sulphurous anhydride with one of oxygen is passed over heated spongy platinum, sulphuric anhydride is formed:

$$\underset{\text{Sulphurous anhydride.}}{SO_2} + O = \underset{\text{Sulphuric anhydride.}}{SO_3}.$$

The sulphuric anhydride condenses in a cooled receiver in the form of fine white needles. The platinum appears to undergo no change in the process, and may be used for any length of time.

The above reaction has been elaborated into an ingenious manufacturing process. The mixture of gases is obtained from concentrated sulphuric acid, which is allowed to fall drop by drop on to fragments of red-hot brick, when the following decomposition takes place:

$$\underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Sulphurous anhydride.}}{SO_2} + O + \underset{\text{Water.}}{OH_2}.$$

The mixed gases are freed from water by passing through concentrated sulphuric acid, and are then led over heated spongy platinum as already described.

2. When Nordhausen sulphuric acid (*q.v.*) is gently heated in a retort, sulphuric anhydride distils over, whilst ordinary sulphuric acid is left:

$$\underset{\text{Nordhausen sulphuric acid.}}{\left\{\begin{array}{l} SO_2Ho \\ O \\ SO_2Ho \end{array}\right.} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Sulphuric anhydride.}}{SO_3}.$$

3. A similar reaction takes place when the so-called anhydrous sodic bisulphate (disodic disulphate, sodic pyrosulphate), a salt of Nordhausen sulphuric acid, is heated. This sodic pyrosulphate is prepared by heating hydric sodic sulphate to low redness, two molecules of the latter salt parting with one of water:

$$\underset{\text{Hydric sodic sulphate.}}{2SO_2HoNao} = \underset{\text{Sodic pyrosulphate.}}{\left\{\begin{array}{l} SO_2Nao \\ O \\ SO_2Nao \end{array}\right.} + \underset{\text{Water.}}{OH_2}$$

When the pyrosulphate is heated to bright redness it is decomposed as follows:

$$\underset{\text{Sodic pyrosulphate.}}{\left\{\begin{array}{l} SO_2Nao \\ O \\ SO_2Nao \end{array}\right.} = \underset{\text{Sodic sulphate.}}{SO_2Nao_2} + \underset{\text{Sulphuric anhydride.}}{SO_3}.$$

4. Sulphuric anhydride may also be prepared by directly abstracting the elements of water from sulphuric acid by heating it with phosphoric anhydride:

$$\underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Phosphoric anhydride.}}{P_2O_5} = \underset{\text{Sulphuric anhydride.}}{SO_3} + \underset{\text{Metaphosphoric acid.}}{2PO_2Ho.}$$

Properties.—Sulphuric anhydride is capable of existing in two distinct modifications. When the melted anhydride is rapidly cooled, it begins to solidify at 16° C, forming long transparent colorless prisms, which fuse again at the same temperature. This modification is sometimes distinguished as the α anhydride. If, however, the liquefied substance be kept for some time at a temperature of 25° C. (77° F.), the whole gradually solidifies to a tangled mass of fine white needles. These needles liquefy gradually at a temperature above 50° C. (122° F.), without possessing a constant fusing-point, and when once liquefied may be converted into the α andydride by cooling to 16° C. (60.8° F.). This second variety is distinguished as the β anhydride.

Liquid sulphuric anhydride possesses between the temperatures of 25° and 45° C. (77–113° F.) a mean co-efficient of expansion of 0.0027, almost three-fourths of the co-efficient of expansion of gases. At 46° C. (114.8° F.), it boils, and is converted into a colorless vapor. Sulphuric anhydride possesses a considerable vapor-tension at ordinary temperatures and gives off dense white fumes in contact with air, owing to the combination of its vapor with the moisture of the air to form sulphuric acid, a liquid of lower vapor-tension than water.

The same combination takes place when the solid anhydride is thrown into water, the reaction being accompanied with a hissing as of a red-hot iron.

SULPHURIC ACID.

$$SO_2Ho_2.$$

Molecular weight = 98. *Sp. gr.* 1.85. *Boils at* 330° C. (626° F.), *undergoing dissociation into sulphuric anhydride and water.*

History.—Sulphuric acid was known to the alchemists, who prepared it by distilling ferrous sulphate.

Occurrence.—In combination with bases sulphuric acid is found in numerous minerals (p. 243; see also *Sulphates*). In the free state it occurs in volcanic waters, being formed by the oxidation of sulphurous acid.

Preparation.—1. Sulphuric acid is formed by the direct union of sulphurous anhydride with hydroxyl, the sulphur passing from the tetradic into the hexadic condition:

$$\underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Hydroxyl.}}{Ho_2} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2.}$$

2. Dry sulphurous anhydride cannot take up oxygen without the aid of heated spongy platinum or some other substance which can act

as a carrier of oxygen, but in its aqueous solution as sulphurous acid it readily absorbs oxygen from the air, and is converted into sulphuric acid:

$$\underset{\text{Sulphurous acid.}}{SOHo_2} + O = \underset{\text{Sulphuric acid.}}{SO_2Ho_2}.$$

3. It is formed by the addition of water to sulphuric anhydride:

$$\underset{\text{Sulphuric anhydride.}}{SO_3} + \underset{\text{Water.}}{OH_2} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2}.$$

4. By the action of nitric peroxide and oxygen on sulphurous anhydride a peculiar white crystalline compound, known as *crystals of the leaden chamber*, is formed, which, according to Brüning and De la Provostaye, possesses the empirical formula $S_2N_2O_9$:

$$\underset{\text{Sulphurous anhydride.}}{2SO_2} + \underset{\text{Nitric peroxide.}}{'N^{iv}{}_2O_4} + O = \underset{\text{White crystalline compound.*}}{\left\{\begin{array}{l} SO_2(N'''O_2) \\ O \\ SO_2(N'''O_2) \end{array}\right.}.$$

If a small quantity of water is present the compound has the following composition (Weltzien):

$$\underset{\text{Sulphurous anhydride.}}{2SO_2} + \underset{\text{Nitric peroxide.}}{'N^{iv}{}_2O_4} + O + \underset{\text{Water.}}{OH_2} = \underset{\text{Weltzien's crystalline compound.}}{2SO_2(N'''O_2)Ho}.$$

It will be perceived that the first of these substances is an anhydride of the second. Both are compound anhydrides of sulphuric and nitrous acids, and are decomposed by a small quantity of water into sulphuric acid and nitrous anhydride:

$$\underset{\text{White crystalline compound.}}{\left\{\begin{array}{l} SO_2(N'''O_2) \\ O \\ SO_2(N'''O_2) \end{array}\right.} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Sulphuric acid.}}{2SO_2Ho_2} + \underset{\text{Nitrous anhydride.}}{N_2O_3}.$$

In the manufacture of sulphuric acid on the large scale, the reaction takes place in presence of an excess of water, by which the nitrous anhydride is transformed into nitric acid and nitric oxide.

$$* \quad O{=}N{-}O{-}\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}{-}O{-}\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}{-}O{-}N{=}O.$$

$$3N_2O_3 + OH_2 = 2NO_2Ho + 4{}'N''O.$$

Nitrous anhydride.	Water.	Nitric acid.	Nitric oxide.

The nitric oxide combines with oxygen, reproducing nitric peroxide, which is then ready to take part in the same processes a second time. The nitric acid is reduced to nitric peroxide by the action of sulphurous anhydride:

$$SO_2 + 2NO_2Ho = SO_2Ho_2 + {}'N^{iv}{}_2O_4.$$

Sulphurous anhydride.	Nitric acid.	Sulphuric acid.	Nitric peroxide.

The whole of the nitric peroxide has thus, after taking part in this series of reactions, returned to its original condition. Theoretically, therefore, a small quantity of this substance ought to be able to convert an indefinitely great quantity of sulphurous anhydride, oxygen, and water into sulphuric acid. In practice, however, there is considerable loss of nitric peroxide which must be constantly replaced.

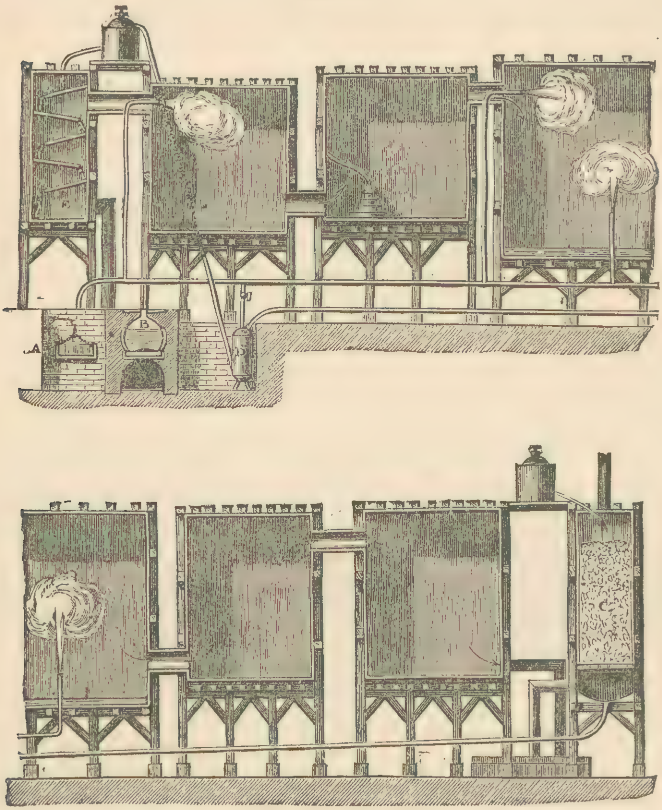
On the above reactions the commercial process for the manufacture of sulphuric acid is founded. The following is a brief outline of the operations:

The sulphurous anhydride is procured by the combustion either of sulphur or of iron pyrites in a furnace *A* (Fig. 42), constructed for this purpose. The gas passes on, mixed with nitrogen and oxygen, into a large leaden chamber, of which there are two or more connected consecutively by means of wide passages. The sheet-lead, of which the walls of these chambers are constructed, is soldered by melting its edges together with the hydrogen blow-pipe. A junction in which any other metal had been employed would not resist corrosion by the sulphuric acid, as a voltaic action would be thus set up with the lead. The gases from the pyrites burners, before entering the chambers, traverse an arrangement, *E*, known as a "Glover's tower." This consists of a tall leaden tower lined with fire-brick and filled with broken flints, or, less frequently, furnished with shelves. At the top of this tower are two reservoirs; one filled with dilute acid from the chambers, the other containing a strong acid saturated with nitric peroxide and derived from the "Gay-Lussac tower" (see p. 270) in a later stage of the process. As the two acids from the reservoirs mix in trickling down over the flints, the nitric peroxide, which is insoluble in dilute acid, is liberated, and is carried by the gases from the pyrites burners into the leaden chamber. At the same time this dilute acid, meeting the hot gases, is deprived of a considerable portion of its water, which is carried into the leaden chamber in the form of steam to furnish the water necessary to the formation of sulphuric acid; and a concentration is thus economically effected.

The oxides of nitrogen required to supply the place of those unavoidably lost during the process, are prepared from a mixture of sodic nitrate and sulphuric acid contained in nitre-pots which are placed at the entrance to the chambers and heated by the pyrites burners. As the mixture of sulphurous anhydride, oxides of nitrogen, and oxygen

passes through the first chamber, the reactions already described (see *Preparation* 4) take place. Jets of steam from the boiler *B* are constantly blown into the chamber, thus furnishing the water necessary for the formation of the acid. In order to save the fuel required for the

Fig. 42.



production of steam, Sprengel recommends that, instead of steam, water, in the form of fine spray, should be blown in. The sulphuric acid collects on the bottom of the chamber, and the liberated oxides of nitrogen pass on into the second chamber. Here the gases meet with a fresh supply of steam, and the sulphurous anhydride which has escaped the reaction in the first chamber is converted into sulphuric acid. Nothing ought to escape from the last chamber but nitric peroxide, an excess of oxygen, and the nitrogen of the air. The nitric peroxide is recovered by passing the spent gases through the Gay-Lussac tower *C*, which is similar in construction to the Glover tower, except that it is filled with fragments of coke. Concentrated sulphuric acid is introduced at the top of this tower and, meeting the nitric peroxide, which is passing in the contrary direction, absorbs it. This acid, saturated with nitric peroxide, is drawn off at the bottom of the tower, and utilized in

the Glover's tower as already described. The circulation of the gases through the chambers is kept up by means of the draught of a tall chimney connected with the Gay-Lussac tower.

The acid is not allowed to attain a specific gravity greater than 1.55 or 1.6 in the chambers, as beyond this point it absorbs oxides of nitrogen. The further concentration is effected partly in the Glover's tower and partly by evaporation in large retorts of glass or platinum.

In practice about 95 per cent. of sulphur is converted into sulphuric acid, and about 2 parts of sodic nitrate are required for every 100 parts of sulphur.

The acid thus prepared contains lead derived from the chambers and arsenic from the pyrites. Nitrous anhydride is also present. This last impurity may be removed by the addition of some ammonic sulphate:

$$\underset{\text{Ammonic sulphate.}}{SO_2(NH_4O)_2} + \underset{\text{Nitrous anhydride.}}{N_2O_3} = \underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Water.}}{3OH_2} + 2N_2.$$

The arsenic may be got rid of by adding hydrochloric acid and boiling, when it passes off as arsenious chloride, along with the excess of hydrochloric acid. The sulphuric acid must finally be purified by re-distillation.

Properties.—Sulphuric acid, concentrated as far as possible by boiling, still retains 1.5 per cent. of water. When this acid is cooled to 0° C., the pure acid of the formula SO_2Ho_2, crystallizes out in colorless prisms fusing at 10.5° C. (50.9° F.). When the pure acid is heated it first gives off sulphuric anhydride, until it contains 1.05 per cent. of water, when it distils unchanged. Ordinary commercial sulphuric acid does not contain more than 94 per cent. of SO_2Ho_2.

Sulphuric acid boils at 330° C. (626° F.), undergoing dissociation into sulphuric anhydride and water, which, however, immediately re-unite when the vapor is condensed. Owing to this dissociation, the vapor-density is only half as great as it would be if no decomposition had taken place:

$$SO_2Ho_2 = \underset{\text{2 vols.}}{SO_3} + \underset{\text{2 vols.}}{OH_2}.$$

(Cf. also p. 64.)

When diluted with water and cooled to 0° it deposits large prismatic crystals of the formula SO_2Ho_2,OH_2, fusing at 7.5° C. This may be regarded as a tetrabasic acid of the formula $SOHo_4$. This is substantially the acid which runs from the Glover's tower, and is known in commerce under the name of "brown acid," having a specific gravity of 1.720. Salts of this tetrabasic acid are known.

A third hydrate, $SO_2Ho_2,2OH_2$, corresponding to a hexabasic acid, SHo_6, was obtained by Graham by evaporating dilute sulphuric acid at 100° C. *in vacuo* till it ceased to lose weight. Salts of this hexabasic acid are also known. The formation of this hydrate also corresponds to the maximum contraction which takes place when sulphuric acid and water are mixed (see below).

Pure dibasic sulphuric acid is a heavy oily colorless liquid. It has a very strong affinity for water. When the two liquids are mixed great heat is evolved, the temperature frequently rising above 100° C. The mixing must be performed gradually, care being taken to pour the acid into the water; if this order be reversed, the hot acid will be thrown about by the explosive ebullition of the water. The mixture is accompanied by diminution of volume: the maximum contraction, amounting to 8 per cent., occurs when 1 molecule of acid is mixed with 2 of water.

The following table contains the specific gravities of aqueous sulphuric acid of various strengths at a temperature of 15° C.:

Specific Gravity Table of Sulphuric Acid at 15° C. (J. Kolb).

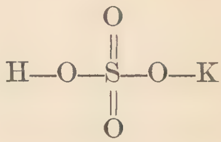
Degrees (Baumé).	Specific gravity at 15°.	Percentage of SO_2Ho_2.	Degrees (Baumé).	Specific gravity at 15°.	Percentage of SO_2Ho_2.
0	1.000	0.9	34	1.308	40.2
1	1.007	1.9	35	1.320	41.6
2	1.014	2.8	36	1.332	43.0
3	1.022	3.8	37	1.345	44.4
4	1.029	4.8	38	1.357	45.5
5	1.037	5.8	39	1.370	46.9
6	1.045	6.8	40	1.383	48.3
7	1.052	7.8	41	1.397	49.8
8	1.060	8.8	42	1.410	51.2
9	1.067	9.8	43	1.424	52.8
10	1.075	10.8	44	1.438	54.0
11	1.083	11.9	45	1.453	55.4
12	1.091	13.0	46	1.468	56.9
13	1.100	14.1	47	1.483	58.3
14	1.108	15.2	48	1.494	59.6
15	1.116	16.2	49	1.514	61.0
16	1.125	17.3	50	1.530	62.5
17	1.134	18.5	51	1.540	64.0
18	1.142	19.6	52	1.563	65.5
19	1.152	20.8	53	1.580	67 0
20	1.162	22 2	54	1.597	68.6
21	1.171	23.3	55	1.615	70.0
22	1.180	24.5	56	1.634	71.6
23	1.190	25.8	57	1.652	73.2
24	1.200	27.1	58	1.671	74.7
25	1.210	28.4	59	1.691	76.4
26	1.220	29.6	60	1.711	78.1
27	1.231	31.0	61	1.732	79.9
28	1.241	32.2	62	1.753	81.7
29	1.252	33.4	63	1.774	84.1
30	1.263	34.7	64	1.796	86 5
31	1.274	36.0	65	1.819	89.7
32	1.285	37.4	66	1.842	100.0
33	1.297	38.8			

Owing to the affinity of sulphuric acid for water, it frequently removes the elements of water from organic compounds. In this way oxalic acid $\left(\left\{\begin{matrix}COHo\\COHo\end{matrix}\right)\right.$ is decomposed into carbonic anhydride, carbonic oxide, and water (p. 209. Sugar, wood, and other substances

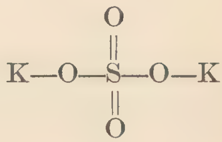
belonging to the class of the *carbohydrates*, so called because the oxygen and hydrogen which they contain in combination with carbon are present in the proportions necessary to form water, are charred by the action of strong sulphuric acid. Its powerfully corrosive action on the animal tissues is due to the same cause.

Sulphates.—Sulphuric acid forms several classes of salts, of which the following compounds may be taken as typical examples:

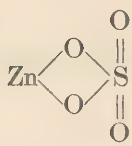
Hydric potassic sulphate, . $\mathbf{S}O_2HoKo$.



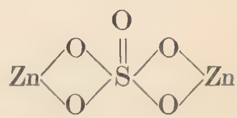
Potassic sulphate, . . . $\mathbf{S}O_2Ko_2$.



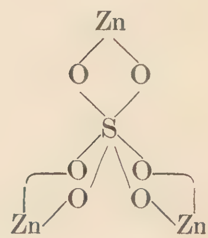
Zincic sulphate, ... $\mathbf{S}O_2Zno''$.



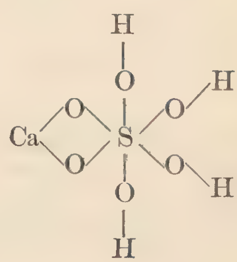
Tetrabasic zincic sulphate. (*Dizincic sulphate.*) . . $\mathbf{S}OZno''_2$.



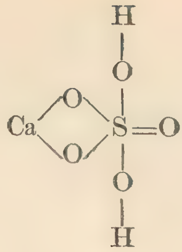
Hexabasic zincic sulphate. (*Trizincic sulphate.*) . . $\mathbf{S}Zno''_3$.



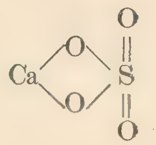
Crystallized gypsum. (*Tetrahydric calcic sulphate.*) $\mathbf{S}Ho_4Cao''$.



Gypsum dried at 100° C. (*Dihydric calcic sulphate.*) $\Big\}$ $SOHo_2Cao''$.



Gypsum dried at 200° C. (*Calcic sulphate.*) . . . $\Big\}$ SO_2Cao''.



The sulphates of barium and lead are insoluble in water; those of calcium, strontium, and silver sparingly soluble; all other normal sulphates are readily soluble.

PYROSULPHURIC ACID. *Dihydric Disulphate. Nordhausen Sulphuric Acid.*

$$\begin{cases} SO_2Ho \\ O \\ SO_2Ho \end{cases} .$$

Preparation.—1. This compound is formed by the action of sulphuric oxychlorhydrate on sulphuric acid:

$$\underset{\text{Sulphuric oxychlorhydrate.}}{SO_2ClHo} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Pyrosulphuric acid.}}{\begin{cases} SO_2Ho \\ O \\ SO_2Ho \end{cases}} + \underset{\text{Hydrochloric acid.}}{HCl.}$$

2. Sulphuric anhydride is dissolved by concentrated sulphuric acid, with formation of pyrosulphuric acid:

$$\underset{\text{Sulphuric acid.}}{SO_2Ho_2} + \underset{\text{Sulphuric anhydride.}}{SO_3} = \underset{\text{Pyrosulphuric acid.}}{\begin{cases} SO_2Ho \\ O \\ SO_2Ho \end{cases}} .$$

The result of the reaction is a strongly fuming liquid, which, when cooled to 0° C., deposits the pyrosulphuric acid in the form of large colorless crystals, fusing at 35° C. (95° F.). On heating, pyrosulphuric acid is decomposed into sulphuric acid and sulphuric anhydride.

3. It is prepared on a large scale by distilling dried ferrous sulphate

in earthenware retorts. The ferrous sulphate is decomposed into ferric oxide, sulphurous and sulphuric anhydrides:

$$\underset{\text{Ferrous sulphate.}}{2\mathbf{S}O_2Feo''} = \underset{\text{Ferric oxide.}}{\mathbf{Fe}_2O_3} + \underset{\text{Sulphurous anhydride.}}{\mathbf{S}O_2} + \underset{\text{Sulphuric anhydride.}}{\mathbf{S}O_3}.$$

Crystallized ferrous sulphate has the formula $\mathbf{S}OHo_2Feo'',6OH_2$. It parts with its water of crystallization at 100° C.; but in order to convert the resulting compound $\mathbf{S}OHo_2Feo''$ into $\mathbf{S}O_2Feo''$ and water, a much higher temperature is necessary, and in practice it is found impossible completely to dehydrate large quantities of the salt. Water is therefore given off in the distillation of the ferrous sulphate, and combines with the sulphuric anhydride to form the fuming acid. The presence of sulphurous anhydride is objectionable, as this gas, in escaping, carries away with it considerable quantities of the volatile sulphuric anhydride. The water and the sulphurous anhydride are, however, chiefly given off in the earlier part of the process. This process takes place in two stages. In the first of these the dihydric ferrous sulphate is converted, with evolution of sulphurous anhydride and water, into diferric sulphate—a compound derived from the hexabasic acid:

$$\underset{\text{Dihydric ferrous sulphate.}}{2\mathbf{S}OHo_2Feo''} = \underset{\text{Diferric sulphate.}}{\mathbf{S}('Fe'''_2O_6)^{vi}} + \underset{\text{Sulphurous anhydride.}}{\mathbf{S}O_2} + \underset{\text{Water.}}{2OH_2}.$$

In the second stage the diferric sulphate breaks up into sulphuric anhydride, which distils over, and ferric oxide, which remains in the retort:

$$\underset{\text{Diferric sulphate.}}{\mathbf{S}('Fe'''_2O_6)^{vi}} = \underset{\text{Sulphuric anhydride.}}{\mathbf{S}O_3} + \underset{\text{Ferric oxide.}}{'\mathbf{Fe}'''_2O_3}.$$

The first portion of the distillate, consisting of a weak acid, is therefore rejected, and the product is only collected when the white fumes of the anhydride begin to make their appearance. The resulting brownish liquid is the *Nordhausen sulphuric acid* of commerce. The production of sulphurous anhydride may be greatly reduced, and the yield of sulphuric anhydride correspondingly increased, by a preliminary oxidation of the ferrous sulphate to ferric sulphate. This is accomplished by drying the ferrous salt at a relatively high temperature with free access of air.

Character.—Pyrosulphuric acid may be regarded as derived from two molecules of sulphuric acid by the abstraction of one molecule of water:

$$\underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2} - \underset{\text{Water.}}{OH_2} = \underset{\text{Pyrosulphuric acid.}}{\left\{\begin{matrix}\mathbf{S}O_2Ho\\ O\\ \mathbf{S}O_2Ho\end{matrix}\right.}.$$

It is thus a semi-anhydride, possessing the properties both of an anhydride and of an acid. If it were possible for the molecule of

pyrosulphuric acid to part with a second molecule of water, we should obtain an anhydride, , the true anhydride of pyrosulphuric acid, polymeric with ordinary sulphuric anhydride, SO_3. It is possible that the modification of sulphuric anhydride melting above 50° corresponds with this anhydride of higher molecular weight.

The formation of sodic pyrosulphate has already been described (p. 266).

PERSULPHURIC ANHYDRIDE.

S_2O_7.

Preparation.—This compound, discovered by Berthelot, was prepared by subjecting a mixture of equal volumes of sulphurous anhydride and oxygen to the action of the silent electric discharge of a Siemens tube (p. 166). At the end of ten hours the substance was thus obtained in the form of drops of a syrupy liquid, which at 0° solidified to needles resembling those of sulphuric anhydride.

Properties.—Persulphuric anhydride dissolves in water, but the solution is almost instantly decomposed into sulphuric acid and free oxygen.

$$S_2O_7 + 2OH_2 = 2SO_2Ho_2 + O.$$

The solution in concentrated sulphuric acid is more stable, but slowly evolves oxygen. The addition of spongy platinum to the solution causes the oxygen to be given off at once.

Persulphuric anhydride is an oxidizing agent. It converts ferrous into ferric salts, and oxidizes sulphurous to sulphuric anhydride.

With baryta water it yields baric persulphate, which is soluble in water, but the solution speedily deposits insoluble baric sulphate with evolution of oxygen.

THIOSULPHURIC ACID (formerly termed *Hyposulphurous Acid*).

SO_2HoHs (hypothetical).

This acid is not known in the free state, as, when liberated from its salts, it almost instantly undergoes decomposition (see below).

Preparation of Thiosulphates (*formerly Hyposulphites*).—1. Sodic thiosulphate is formed when a solution of sulphite is boiled with flowers of sulphur:

$$\underset{\text{Sodic sulphite.}}{SONao_2} + S = \underset{\text{Sodic thiosulphate.}}{SO_2NaoNas.}$$

This formula for sodic thiosulphate is true of the salt only after exposure to a temperature of 215° C. (419° F.). The composition of the salt when dried at a lower temperature is $SOHo_2NaoNas$. This peculiarity of containing a molecule of water of constitution which can be expelled only at a high temperature, and, in many cases, not without decomposition of the salt, is shared by most of the other thiosulphates; but plumbic thiosulphate contains no hydrogen, and, after drying at 100° C., has the formula $SO_2\left(\begin{matrix}O\\S\end{matrix}Pb\right)''$.

2. Sodic thiosulphate may also be obtained by passing sulphurous

anhydride into a solution of sodic sulphide. The reaction in this case is of a complex character. First, the sulphurous acid decomposes the alkaline sulphide, yielding sodic sulphite and liberating sulphur, which acts upon the sodic sulphite according to (1), forming sodic trisulphate. The equations are:

$$\underset{\text{Sulphurous acid.}}{3\mathbf{S}\mathrm{OHo_2}} + \underset{\text{Sodic sulphide.}}{2\mathbf{S}\mathrm{Na_2}} = \underset{\text{Sodic sulphite.}}{2\mathbf{S}\mathrm{ONao_2}} + 3\mathrm{S} + \underset{\text{Water.}}{3\mathbf{O}\mathrm{H_2}}.$$

$$\underset{\text{Sodic sulphite.}}{\mathbf{S}\mathrm{ONao_2}} + \mathrm{S} = \underset{\text{Sodic thiosulphate.}}{\mathbf{S}\mathrm{O_2NaoNas}}.$$

3. When sulphur is warmed with a solution of caustic soda, a mixture of sulphide and thiosulphate is formed:

$$\underset{\text{Sodic hydrate.}}{6\mathrm{NaHo}} + 4\mathrm{S} = \underset{\text{Sodic thiosulphate.}}{\mathbf{S}\mathrm{O_2NaoNas}} + \underset{\text{Sodic sulphide.}}{2\mathbf{S}\mathrm{Na_2}} + \underset{\text{Water.}}{3\mathbf{O}\mathrm{H_2}}.$$

The sodic sulphide generated in this reaction may be converted into thiosulphate by passing sulphurous anhydride into the solution (*Preparation* 2.).

4. When a persulphide of an alkali or of an alkaline earth is exposed to the air in a moist state, oxygen is absorbed and a thiosulphate is produced:

$$\underset{\text{Calcic persulphide.}}{'\mathbf{S}'_2\mathrm{Ca}} + 3\mathrm{O_3} = \underset{\text{Calcic thiosulphate.}}{\mathbf{S}\mathrm{O_2}\left(\begin{matrix}\mathrm{O}\\ \mathrm{S}\end{matrix}\mathrm{Ca}\right)''}.$$

The calcic sulphide from the soda waste (see soda manufacture) is frequently employed for this purpose. Sometimes instead of oxidizing the soda waste by the action of the air, it is treated with sulphurous anhydride. In either case the calcic thiosulphate is extracted with water, converted into the sodium salt by means of sodic carbonate or sulphate, and purified by crystallization.

5. Sodic thiosulphate is formed by the action of iodine on a solution of sodic sulphide and sodic sulphite:

$$\underset{\text{Sodic sulphide.}}{\mathbf{S}\mathrm{Na_2}} + \underset{\text{Sodic sulphite.}}{\mathbf{S}\mathrm{ONao_2}} + \mathrm{I_2} = \underset{\text{Sodic thiosulphate.}}{\mathbf{S}\mathrm{O_2NaoNas}} + \underset{\text{Sodic iodide.}}{2\mathrm{NaI}}.$$

Reactions.—1. The thiosulphates, when acted upon by acids, evolve sulphurous anhydride, whilst sulphur is precipitated:

$$\underset{\text{Sodic thiosulphate.}}{\mathbf{S}\mathrm{O_2NaoNas}} + \underset{\text{Hydrochloric acid.}}{2\mathrm{HCl}} = \underset{\text{Sodic chloride.}}{2\mathrm{NaCl}} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H_2}} + \mathrm{S} + \underset{\text{Sulphurous anhydride.}}{\mathbf{S}\mathrm{O_2}}.$$

2. Sodic thiosulphate dissolves argentic chloride, forming a double salt of the formula $\mathbf{S}\mathrm{OHo_2NaoAgs}$:

$$\underset{\text{Sodic thiosulphate.}}{\mathbf{S}O_2NaoNas} + \underset{\text{Argentic chloride.}}{AgCl} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Sodic chloride.}}{NaCl} + \underset{\text{Sodic argentic thiosulphate.}}{\mathbf{S}OHo_2NaoAgs.}$$

It is this property which has led to the employment of sodic thiosulphate in photography as a means of fixing photographs. The photographic paper, sensitized by impregnation with argentic chloride, is blackened in those parts which are exposed to the action of light. In order to render permanent the picture thus produced, it is necessary to remove the unaltered argentic chloride, and this is accomplished by steeping the picture in a bath of sodic thiosulphate.

DITHIONOUS ACID, *Hydrosulphurous Acid.*

$$\left\{\begin{matrix}\mathbf{S}OHo \\ \mathbf{S}OHo\end{matrix}\right.*$$

Preparation.—When zinc is introduced into an aqueous solution of sulphurous anhydride in a vessel from which air is excluded, the metal unites directly with the anhydride to form zincic dithionite:

$$\underset{\text{Sulphurous anhydride.}}{2\mathbf{S}O_2} + Zn = \underset{\text{Zincic dithionite.}}{\left\{\begin{matrix}\mathbf{S}O \\ \mathbf{S}O\end{matrix}\right.Zno.}$$

or if we assume the presence of sulphurous acid in the liquid:

$$\underset{\text{Sulphurous acid.}}{2\mathbf{S}OHo_2} + Zn = \underset{\text{Zincic dithionite.}}{\left\{\begin{matrix}\mathbf{S}O \\ \mathbf{S}O\end{matrix}\right.Zno''} + \underset{\text{Water.}}{OH_2.}$$

Reaction.—The yellow liquid obtained by the above process possesses powerful reducing properties. When exposed to the air, it absorbs oxygen rapidly with great evolution of heat, the dithionous acid being converted into sulphurous acid:

$$\underset{\text{Dithionous acid.}}{\left\{\begin{matrix}\mathbf{S}OHo \\ \mathbf{S}OHo\end{matrix}\right.} + O + \underset{\text{Water.}}{OH_2} = \underset{\text{Sulphurous acid.}}{2\mathbf{S}OHo_2.}$$

It also precipitates silver and mercury in the metallic state from the solutions of their salts.

Schützenberger has proposed to use it for the estimation of dissolved oxygen in water.

DITHIONIC ACID, *Hyposulphuric Acid.*

$$\left\{\begin{matrix}\mathbf{S}O_2Ho \\ \mathbf{S}O_2Ho\end{matrix}\right..$$

Preparation.—1. Powdered manganic oxide is suspended in water and a current of sulphurous anhydride is passed through the liquid, when the manganic oxide gradually dissolves. The solution contains manganous dithionate:

$$\underset{\text{Manganic oxide.}}{MnO_2} + \underset{\text{Sulphurous anhydride.}}{2\mathbf{S}O_2} = \underset{\text{Manganous dithionate.}}{\left\{\begin{matrix}\mathbf{S}O_2 \\ \mathbf{S}O_2\end{matrix}\right.Mno''.}$$

This solution is next treated with baric sulphide, which precipitates manganous sulphide, whilst baric dithionate is formed and remains in solution:

* The formula $\mathbf{S}OHHo$ was formerly erroneously assigned to this acid.

$$\underset{\text{Manganous dithionate.}}{\left\{\begin{matrix} SO_2 \\ SO_2 \end{matrix}\right. Mno''} + \underset{\text{Baric sulphide.}}{BaS''} = \underset{\text{Manganous sulphide.}}{MnS''} + \underset{\text{Baric dithionate.}}{\left\{\begin{matrix} SO_2 \\ SO_2 \end{matrix}\right. Bao''}.$$

By adding sulphuric acid to a solution of the baric dithionate, baric sulphate is precipitated, and dithionic acid remains in solution:

$$\underset{\text{Baric dithionate.}}{\left\{\begin{matrix} SO_2 \\ SO_2 \end{matrix}\right. Bao''} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Baric sulphate.}}{SO_2Bao''} + \underset{\text{Dithionic acid.}}{\left\{\begin{matrix} SO_2Ho \\ SO_2Ho \end{matrix}\right.}.$$

The solution of dithionic acid may be evaporated *in vacuo* over sulphuric acid till it attains a specific gravity of 1.347, but beyond this point it decomposes into sulphuric acid and sulphurous anhydride. The dilute acid undergoes the same change on boiling.

2. Dithionic acid is also formed when a dilute solution of iodine in potassic iodide is added to a dilute solution of hydric sodic sulphite:

$$\underset{\text{Hydric sodic sulphite.}}{2SOHoNao} + I_2 = \underset{\text{Dithionic acid.}}{\left\{\begin{matrix} SO_2Ho \\ SO_2Ho \end{matrix}\right.} + \underset{\text{Sodic iodide.}}{2NaI}.$$

About 20 per cent. of the sulphite is thus transformed. The remainder is converted into sulphate.

Dithionates.—The dithionates mostly crystallize well. They may be obtained either by neutralizing a solution of the acid with a base, or by exactly precipitating a solution of baric dithionate with a soluble sulphate.

TRITHIONIC ACID, *Sulphodithionic Acid, Sulphuretted Hyposulphuric Acid.*

$$\left\{\begin{matrix} SO_2Ho \\ S'' \\ SO_2Ho \end{matrix}\right. .$$

Preparation.—1. By digesting flowers of sulphur at a temperature of between 50° and 60° C. with a concentrated solution of hydric potassic sulphite, potassic trithionate and potassic thiosulphate are formed:

$$\underset{\text{Hydric potassic sulphite.}}{6SOKoHo} + 2S = \underset{\text{Potassic trithionate.}}{2\left\{\begin{matrix} SO_2Ko \\ S'' \\ SO_2Ko \end{matrix}\right.} + \underset{\text{Potassic thiosulphate.}}{SO_2KoKs} + \underset{\text{Water.}}{3OH_2}.$$

2. Potassic trithionate may also be obtained by saturating a very concentrated solution of potassic thiosulphate with sulphurous anhydride:

$$\underset{\text{Potassic thiosulphate.}}{2SO_2KoKs} + \underset{\text{Sulphurous anhydride.}}{3SO_2} = \underset{\text{Potassic trithionate.}}{2\left\{\begin{matrix} SO_2Ko \\ S'' \\ SO_2Ko \end{matrix}\right.} + S.$$

3. The same salt is formed when a solution of potassic argentic thiosulphate is boiled:

$$\underset{\text{Potassic argentic thiosulphate.}}{2SO_2KoAgs} = \underset{\text{Potassic trithionate.}}{\left\{\begin{matrix} SO_2Ko \\ S'' \\ SO_2Ko \end{matrix}\right.} + \underset{\text{Argentic sulphide.}}{SAg_2}.$$

4. By adding iodine to a solution of sodic sulphite and thiosulphate, sodic trithionate and sodic iodide are formed:

$$\underset{\text{Sodic sulphite.}}{\mathbf{S}\mathrm{ONao_2}} + \underset{\text{Sodic thiosulphate.}}{\mathbf{S}\mathrm{O_2NaoNas}} + \mathrm{I_2} = \underset{\text{Sodic trithionate.}}{\left\{\begin{array}{l}\mathbf{S}\mathrm{O_2Nao}\\ \mathrm{S''}\\ \mathbf{S}\mathrm{O_2Nao}\end{array}\right.} + \underset{\text{Sodic iodide.}}{\mathrm{2NaI}.}$$

An aqueous solution of trithionic acid may be obtained by decomposing the potassium salt with hydrofluosilicic acid:

$$\underset{\text{Potassic trithionate.}}{\left\{\begin{array}{l}\mathbf{S}\mathrm{O_2Ko}\\ \mathrm{S''}\\ \mathbf{S}\mathrm{O_2Ko}\end{array}\right.} + \underset{\text{Hydrofluosilicic acid.}}{\mathbf{Si}\mathrm{F_4,2HF}} = \underset{\text{Trithionic acid.}}{\left\{\begin{array}{l}\mathbf{S}\mathrm{O_2Ho}\\ \mathrm{S''}\\ \mathbf{S}\mathrm{O_2Ho}\end{array}\right.} + \underset{\text{Potassic silicofluoride.}}{\mathbf{Si}\mathrm{F_4,2KF}.}$$

The liquid is filtered from the insoluble potassic silicofluoride. The free acid is very unstable, and spontaneously decomposes into sulphuric acid, sulphurous anhydride, and free sulphur:

$$\underset{\text{Trithionic acid.}}{\left\{\begin{array}{l}\mathbf{S}\mathrm{O_2Ho}\\ \mathrm{S''}\\ \mathbf{S}\mathrm{O_2Ho}\end{array}\right.} = \underset{\text{Sulphuric acid.}}{\mathbf{S}\mathrm{O_2Ho_2}} + \underset{\text{Sulphurous anhydride.}}{\mathbf{S}\mathrm{O_2}} + \mathrm{S}.$$

Sodium amalgam converts a trithionate into a mixture of sulphite and thiosulphate, thus reversing the process of its formation from these salts:

$$\underset{\text{Sodic trithionate.}}{\left\{\begin{array}{l}\mathbf{S}\mathrm{O_2Nao}\\ \mathrm{S''}\\ \mathbf{S}\mathrm{O_2Nao}\end{array}\right.} + \mathrm{Na_2} = \underset{\text{Sodic sulphite.}}{\mathbf{S}\mathrm{ONao_2}} + \underset{\text{Sodic thiosulphate.}}{\mathbf{S}\mathrm{O_2NaoNas}.}$$

TETRATHIONIC ACID, *Disulphodithionic Acid, Bisulphuretted Hyposulphuric Acid.*

$$\left\{\begin{array}{l}\mathbf{S}\mathrm{O_2Ho}\\ \mathrm{S''}\\ \mathrm{S''}\\ \mathbf{S}\mathrm{O_2Ho}\end{array}\right.$$

Preparation.—When iodine is added to a solution of a thiosulphate, an iodide and a tetrathionate of the base are formed:

$$\underset{\text{Sodic thiosulphate.}}{\mathrm{2}\mathbf{S}\mathrm{O_2NaoNas}} + \mathrm{I_2} = \underset{\text{Sodic tetrathionate.}}{\left\{\begin{array}{l}\mathbf{S}\mathrm{O_2Nao}\\ \mathrm{S''}\\ \mathrm{S''}\\ \mathbf{S}\mathrm{O_2Nao}\end{array}\right.} + \underset{\text{Sodic iodide.}}{\mathrm{2NaI}.}$$

This action of iodine, in coupling together two atoms of sulphur in two molecules of substances containing the group Hs (or its equivalent, Ks, Nas, etc.) is characteristic of this element, and meets with many applications in organic chemistry.

If baric thiosulphate be employed, baric tetrathionate will be formed, and by decomposing this salt with dilute sulphuric acid an aqueous solution of tetrathionic acid may be obtained. The dilute solution may be boiled without decomposition; but, when concentrated, the acid breaks up into sulphurous acid, sulphuric acid, and free sulphur.

Sodium amalgam reconverts the tetrathionates into thiosulphates:

$$\underset{\text{Sodic tetrathionate.}}{\left\{\begin{array}{l}\mathbf{S}\mathrm{O_2Nao}\\ \mathrm{S''}\\ \mathrm{S''}\\ \mathbf{S}\mathrm{O_2Nao}\end{array}\right.} + \mathrm{Na_2} = \underset{\text{Sodic thiosulphate.}}{\mathrm{2}\mathbf{S}\mathrm{O_2NaoNas}.}$$

PENTATHIONIC ACID, *Trisulphodithionic Acid, Trisulphuretted Hyposulphuric Acid.*

$$\left\{\begin{array}{l}\mathbf{S}O_2Ho\\ S''\\ S''\\ S''\\ \mathbf{S}O_2Ho\end{array}\right. .$$

Preparation.—1. This acid may be obtained by passing sulphuretted hydrogen into a solution of sulphurous anhydride:

$$\underset{\text{Sulphuretted hydrogen.}}{5\mathbf{S}H_2} + \underset{\text{Sulphurous anhydride.}}{5\mathbf{S}O_2} = \underset{\text{Pentathionic acid.}}{\left\{\begin{array}{l}\mathbf{S}O_2Ho\\ S''\\ S''\\ S''\\ \mathbf{S}O_2Ho\end{array}\right.} + \underset{\text{Water.}}{4\mathbf{O}H_2} + 5S.$$

2. It is also formed by the action of disulphur dichloride on baric thiosulphate:

$$\underset{\text{Baric thiosulphate.}}{2\mathbf{S}O_2{}^{O}_{S}Ba} + \underset{\text{Disulphur dichloride.}}{{}'\mathbf{S}'_2Cl_2} = \underset{\text{Baric pentathionate.}}{\left\{\begin{array}{l}\mathbf{S}O_2-\\ S''\\ S''\ \ Bao''\\ S''\\ \mathbf{S}O_2-\end{array}\right.} + \underset{\text{Baric chloride.}}{\mathbf{Ba}Cl_2} + S.$$

The aqueous solution of the acid may be concentrated till it attains a specific gravity of 1.6, but beyond this point it decomposes, evolving sulphurous anhydride. The pentathionates are unstable, and have been but imperfectly examined.

COMPOUNDS OF SULPHUR WITH OXYGEN AND CHLORINE (OXYCHLORIDES, ACID CHLORIDES).

These compounds may be regarded as derived from the corresponding oxy-acids of sulphur by the substitution of chlorine for hydroxyl (see acid chlorides of the nitrogen acids, p. 229).

Acid chloride.		Corresponding acid.	
Sulphurous oxychloride (*Thionylic chloride*), ...	$\mathbf{S}OCl_2$	Sulphurous acid, . . .	$\mathbf{S}OHo_2$
Sulphuric oxydichloride (*Sulphurylic chloride*), ...	$\mathbf{S}O_2Cl_2$	Sulphuric acid, ...	$\mathbf{S}O_2Ho_2$
Sulphuric oxychlorhydrate (*Sulphurylic chlorhydrate*), ...	$\mathbf{S}O_2ClHo$		
Pyrosulphurylic chloride, ...	$\left\{\begin{array}{l}\mathbf{S}O_2Cl\\ O\\ \mathbf{S}O_2Cl\end{array}\right.$	Pyrosulphuric acid, . .	$\left\{\begin{array}{l}\mathbf{S}O_2Ho\\ O\\ \mathbf{S}O_2Ho\end{array}\right.$

SULPHUROUS OXYDICHLORIDE, *Thionylic Chloride.*

$\mathbf{S}OCl_2$.

Molecular weight = 119. *Molecular volume* $\boxed{}\boxed{}$. 1 *litre of sulphurous oxydichloride vapor weighs* 59.5 *criths. Specific gravity of liquid* 1.675. *Boils at* 78° C. (172.4° F.).

Preparation.—1. When dry sulphurous anhydride is passed over phosphoric chloride, sulphurous oxydichloride and phosphoric oxytrichloride are formed:

$$\underset{\text{Sulphurous anhydride.}}{\mathbf{S}O_2} + \underset{\text{Phosphoric chloride.}}{\mathbf{P}Cl_5} = \underset{\text{Sulphurous oxydichloride.}}{\mathbf{S}OCl_2} + \underset{\text{Phosphoric oxytrichloride.}}{\mathbf{P}OCl_3}.$$

2. It may also be obtained by heating together calcic sulphite and phosphoric oxytrichloride in sealed tubes to 150° C. (302° F.)

$3SOCao''$	+	$2POCl_3$	=	$3SOCl_2$	+	$\left\{\begin{matrix}PO\\PO\end{matrix}\right.Cao''_3.$
Calcic sulphite.		Phosphoric oxytrichloride.		Sulphurous oxydichloride.		Calcic phosphate.

Properties.—Sulphurous oxydichloride is a colorless liquid, possessing a pungent odor.

Reaction.—Water gradually decomposes sulphurous oxydichloride into sulphurous and hydrochloric acids:

$SOCl_2$	+	$2OH_2$	=	$SOHo_2$	+	$2HCl.$
Sulphurous oxychloride.		Water.		Sulphurous acid.		Hydrochloric acid.

SULPHURIC OXYDICHLORIDE, *Sulphurylic Chloride.*

$$SO_2Cl_2.$$

Molecular weight = 135. *Molecular volume* $\square\square$. 1 *litre of sulphuric oxydichloride vapor weighs* 67.5 *criths. Specific gravity of liquid* 1.66. *Boils at* 70° C. (158° F.).

Preparation.—1. Sulphuric oxydichloride is formed by the direct union of sulphurous anhydride and chlorine, either in sunlight or when the two gases are passed into glacial acetic acid or through camphor which immediately liquefies, and the saturated solution, after standing for some time, subjected to distillation:

SO_2	+	Cl_2	=	$SO_2Cl_2.$
Sulphurous anhydride.				Sulphuric oxydichloride.

2. It may also be prepared by heating sulphuric oxychlorhydrate (see below) in sealed tubes for 12 hours to a temperature of from 170° to 180° C. (338°–356° F.).

$2SO_2ClHo$	=	SO_2Cl_2	+	$SO_2Ho_2.$
Sulphuric oxychlorhydrate.		Sulphuric oxydichloride.		Sulphuric acid.

Properties.—Sulphuric oxydichloride is a colorless fuming liquid with a suffocating odor.

Reactions.—1. A small qnantity of water decomposes it into sulphuric oxychlorhydrate and hydrochloric acid:

SO_2Cl_2	+	OH_2	=	SO_2ClHo	+	$HCl.$
Sulphuric oxydichloride.		Water.		Sulphuric oxychlorhydrate.		Hydrochloric acid.

2. An excess of water converts it into sulphuric and hydrochloric acids:

SO_2Cl_2	+	$2OH_2$	=	SO_2Ho_2	+	$2HCl.$
Sulphuric oxydichloride.		Water.		Sulphuric acid.		Hydrochloric acid.

SULPHURIC OXYCHLORHYDRATE, *Sulphurylic Chlorhydrate.*

$$SO_2ClHo.$$

Molecular weight = 116.5. *Molecular volume* $\square\square$. 1 *litre of sulphuric oxychlorhydrate vapor weighs* 58.25 *criths. Specific gravity of liquid* 1.776 *at* 18° C. (64.4° F.). *Boils at* 158° C. (316.4° F.).

Preparation.—1. Sulphuric anhydride and hydrochloric acid unite directly to form sulphuric oxychlorhydrate:

$$SO_3 + HCl = SO_2ClHo.$$

Sulphuric anhydride.	Hydrochloric acid.	Sulphuric oxychlorhydrate.

2. It may be obtained by distilling a mixture of sulphuric acid and phosphoric chloride.

$$3SO_2Ho_2 + PCl_5 = 3SO_2ClHo + PO_2Ho + 2HCl.$$

Sulphuric acid.	Phosphoric chloride.	Sulphuric oxychlorhydrate.	Metaphosphoric acid.	Hydrochloric acid.

Properties.—Sulphuric oxychlorhydrate is a colorless, strongly fuming liquid. When distilled it undergoes partial dissociation into sulphuric anhydride and hydrochloric acid.

Reaction.—Water decomposes it with violence, forming sulphuric and hydrochloric acids:

$$SO_2ClHo + OH_2 = SO_2Ho_2 + HCl.$$

Sulphuric oxychlorhydrate.	Water.	Sulphuric acid.	Hydrochloric acid.

PYROSULPHURYLIC CHLORIDE.

$$\left\{\begin{array}{l} SO_2Cl \\ O \\ SO_2Cl \end{array}\right.$$

Molecular weight = 215. *Molecular volume* $\square\square$. 1 *litre of pyrosulphurylic chloride vapor weighs* 107.5 *criths. Specific gravity of liquid* 1.819 *at* 18° C. (64.4° F.). *Boils at* 146° C. (294.8° F.).

Preparation.—1. This compound is formed when sulphuric anhydride is heated with phosphoric chloride:

$$2SO_3 + PCl_5 = \left\{\begin{array}{l} SO_2Cl \\ O \\ SO_2Cl \end{array}\right. + POCl_3.$$

Sulphuric anhydride.	Phosphoric chloride.	Pyrosulphurylic chloride.	Phosphoric oxytrichloride.

2. It is also produced by the action of disulphur dichloride on sulphuric anhydride:

$$'S'_2Cl_2 + 5SO_3 = \left\{\begin{array}{l} SO_2Cl \\ O \\ SO_2Cl \end{array}\right. + 5SO_2.$$

Disulphur dichloride.	Sulphuric anhydride.	Pyrosulphurylic chloride.	Sulphurous anhydride.

Properties.—Pyrosulphurylic chloride is a heavy, colorless, fuming liquid.

Reaction.—In contact with water it is slowly decomposed into sulphuric and hydrochloric acids:

$$\left\{\begin{array}{l} SO_2Cl \\ O \\ SO_2Cl \end{array}\right. + 3OH_2 = 2SO_2Ho_2 + 2HCl.$$

Pyrosulphurylic chloride.	Water.	Sulphuric acid.	Hodrochloric acid.

SELENIUM, Se_2.

Atomic weight = 79. *Molecular weight* = 158. *Molecular volume* $\square\square$. 1 *litre of selenium vapor weighs* 79 *criths. Sp. gr., amorphous,* 4.28; *crystallized,* 4.8. *Fuses at* 217° C. (422.6° F.). *Boils about* 700° C. (1292° F.). *Atomicity* ″, ^{iv}, *and* ^{vi}. *Evidence of atomicity:*

Seleniuretted hydrogen, ...	$Se''H_2$.
Selenious chloride, ...	$Se^{iv}Cl_4$.
Selenic acid, ...	$Se^{vi}O_2Ho_2$.

History.—Selenium (from σελήνη, the moon) was discovered in 1817 by Berzelius in a deposit from a sulphuric acid chamber. The name

was given on account of the analogy of this element with tellurium (*tellus*, the earth).

Occurrence.—Selenium is generally found in very small quantities along with sulphur, both native and combined. Less frequently it occurs alone in combination with metals in a few rare minerals, as the selenides of lead, copper, silver, and mercury.

When iron- or copper-pyrites containing selenium is employed in the manufacture of sulphuric acid, the selenium forms a red deposit in the chambers.

Preparation.—The red deposit from the sulphuric acid chambers is digested with a warm solution of potassic cyanide until the red color disappears. Soluble potassic selenocyanide is formed:

$$\underset{\text{Potassic cyanide.}}{KCy} + Se = \underset{\text{Potassic selenocyanide.}}{\mathbf{Se}KCy.}$$

On adding an excess of hydrochloric acid to the filtered solution, selenium is precipitated as a red amorphous powder, the liberated selenocyanic acid being instantly decomposed in presence of strong acids into hydrocyanic acid, which remains in solution, and selenium.

Properties.—Selenium, like sulphur, exists in various modifications. When precipitated from solutions by means of acids, it forms an amorphous brick-red powder, which, when heated along with the liquid, turns black and cakes together below 100° C. When melted and rapidly cooled, selenium solidifies to a black, shining, amorphous mass, with a conchoidal fracture. This variety is soluble in carbonic disulphide, and possesses a specific gravity of 4.28. The solution deposits monoclinic crystals, isomorphous with those of monoclinic sulphur. The fusing point of soluble selenium cannot be determined, as this substance softens gradually on heating.

When amorphous selenium is heated for some time to a temperature of 97° C. (206.6° F.), it is converted into the crystalline modification. This change is attended with evolution of great heat, the temperature of the mass rising above 200° C. Crystalline selenium is of a dark gray color, with a metallic lustre and granular fracture. Its specific gravity is 4.5. The same variety is obtained when melted selenium is allowed to cool very slowly. It is insoluble in carbonic disulphide. This modification conducts the electric current. Its electrical resistance is greatly diminished by exposing the substance to light, but is again restored on shading it from the light—a property which is turned to account in the construction of the photophone.

When a solution of an alkaline selenide is exposed to the air, minute black crystals of selenium separate out, possessing a specific gravity of 4.8. They are insoluble in carbonic disulphide.

The vapor-density of selenium, like that of sulphur, decreases as the temperature rises. Above 1400° C. (2552° F.) it possesses the normal vapor-density corresponding with the molecular weight $Se_2 = 158$. The following determinations of the vapor-density (air = 1) illustrate this decrease:

Temperature.	Vapor-density.
860° C. (1580° F.)	7.67
1040° " (1804° ")	6.37
1420° " (2588° ")	5.68

Selenium dissolves in fuming sulphuric acid, with a green color.

Reaction.—When heated in the air selenium burns, forming selenious anhydride, $\mathbf{Se}O_2$, at the same time giving off an odor of decayed horse-radish.

Nitric acid oxidizes selenium to selenious acid, $\mathbf{Se}OHo_2$, whereas sulphur under the same conditions yields sulphuric acid.

COMPOUNDS OF SELENIUM WITH HYDROGEN AND CHLORINE.

SELENIURETTED HYDROGEN, *Hydroselenic Acid.*

$\mathbf{Se}H_2$.

Molecular weight = 81. *Molecular volume* $\square\square$. 1 *litre weighs* 40.5 *criths.*

Preparation.—This compound is formed by the action of dilute hydrochloric acid upon ferrous selenide:

$\mathbf{Fe}Se''$	+	$2HCl$	=	$\mathbf{Se}H_2$	+	$\mathbf{Fe}Cl_2$.
Ferrous selenide.		Hydrochloric acid.		Seleniuretted hydrogen.		Ferrous chloride.

Properties.—Seleniuretted hydrogen is a colorless gas, possessing an odor resembling that of sulphuretted hydrogen, but much more powerful. Inhalation of a single bubble of seleniuretted hydrogen through the nose destroys for some time the sense of smell. Like sulphuretted hydrogen it produces precipitates in solutions of most of the heavy metals. It is decomposed by heat into its elements. The degree of this dissociation varies in a remarkable manner, being less at a higher than at a lower temperature. Thus the dissociation begins at 150° C. (302° F.), increases gradually up to 270° C. (518° F.), then decreases gradually as the temperature rises, till at 520° C. (968° F.) it almost entirely ceases. At still higher temperatures it again increases.

When ignited, seleniuretted hydrogen burns in air with a blue flame, yielding selenious anhydride and water:

$\mathbf{Se}H_2$	+	$3O$	=	$\mathbf{Se}O_2$	+	$\mathbf{O}H_2$.
Seleniuretted hydrogen.				Selenious anhydride.		Water.

There are two chlorides of selenium, $'\mathbf{Se}'_2Cl_2$ and $\mathbf{Se}Cl_4$.

COMPOUNDS OF SELENIUM WITH OXYGEN AND HYDROXYL.

Selenious anhydride, ...	SeO_2.
Selenious acid, ...	$SeOHo_2$.
Selenic acid, ...	SeO_2Ho_2.

SELENIOUS ANHYDRIDE.

SeO_2.

Preparation.—Selenious anhydride is formed by the direct combination of its elements, when selenium is burned in a stream of oxygen.

It may also be obtained by heating selenious acid:

$$\underset{\text{Selenious acid.}}{SeOHo_2} = \underset{\text{Selenious anhydride.}}{SeO_2} + \underset{\text{Water.}}{OH_2}.$$

Properties.—Selenious anhydride crystallizes in prisms, and when heated sublimes without fusing.

Reaction.—Dissolved in water it forms selenious acid by a reaction the reverse of the foregoing.

SELENIOUS ACID.

$SeOHo_2$.

Preparation.—1. As above, by dissolving selenious anhydride in water.

2. It is formed when selenium is oxidized with nitric acid:

$$Se + O_2 + \underset{\text{Water.}}{OH_2} = \underset{\text{Selenious acid.}}{SeOHo_2}.$$

Properties.—Selenious acid is a white, very soluble substance, crystallizing in prisms. It forms normal, acid, and superacid salts:

Normal potassic selenite, ...	$SeOKo_2$.
Hydric potassic selenite, ...	$SeOHoKo$.
Superacid potassic selenite, . . .	$SeOHoKo,SeOHo_2$.

Reaction.—Reducing agents, such as sulphurous acid, stannous chloride, etc., precipitate red amorphous selenium from its solutions:

$$\underset{\text{Selenious acid.}}{SeOHo_2} + \underset{\text{Sulphurous acid.}}{2SOHo_2} = Se + \underset{\text{Sulphuric acid.}}{2SO_2Ho_2} + \underset{\text{Water.}}{OH_2}.$$

SELENIC ACID.

SeO_2Ho_2.

Preparation.—1. The most convenient method of obtaining this acid consists in suspending argentic selenite in water, and adding bromine until a perceptible reddish coloration is visible:

$SeOAgo_2$	$+$	Br_2	$+$	OH_2	$=$	SeO_2Ho_2	$+$	$2AgBr$.
Argentic selenite.				Water.		Selenic acid.		Argentic bromide.

On evaporating the filtered liquid a concentrated solution of selenic acid remains.

2. Potassic seleniate is prepared by fusing selenium or metallic selenides with nitre. The potassic salt thus formed is then converted into a plumbic salt, and, by decomposing the latter with sulphuretted hydrogen, selenic acid is obtained.

Properties.—Selenic acid is not known in a state of purity. The most concentrated aqueous solution contains 97.4 per cent. of the acid. Further evaporation causes it to decompose into selenious anhydride, oxygen, and water. The solution has a specific gravity of 2.627, and closely resembles in its properties concentrated sulphuric acid.

It is remarkable as being the only single acid which dissolves gold. In this process it undergoes reduction to selenious acid.

Reaction.—When heated with hydrochloric acid, selenic acid is reduced to selenious acid, chlorine being liberated:

SeO_2Ho_2	$+$	$2HCl$	$=$	$SeOHo_2$	$+$	OH_2	$+$	Cl_2.
Selenic acid.		Hydrochloric acid.		Selenious acid.		Water.		

Selenic anhydride has not been prepared.

TELLURIUM, Te_2.

Atomic weight = 125. *Molecular weight* = 250. *Molecular volume* $\square\square$. 1 *litre of tellurium vapor weighs* 125 *criths*. *Sp. gr.* 6.2. *Fuses at* 490°–500° C. (914°–932° F.). *Atomicity* $''$, ^{iv}, *and* ^{vi}. *Evidence of atomicity:*

Telluretted hydrogen, ...	$Te''H_2$.
Tellurous chloride, ...	$Te^{iv}Cl_4$.
Telluric acid, ...	$Te^{vi}O_2Ho_2$.

History.—Tellurium (from *tellus*, the earth) was first recognized as a distinct substance by Müller von Reichenstein, in 1782.

Occurrence.—It is found in very small quantities both in the native state and as the tellurides of metals.

Preparation.—Bismuthic telluride, $Bi_2Te''_3$, a substance occurring in

nature as the mineral *tetradymite*, is fused with a mixture of sodic carbonate and finely-powdered charcoal. The fused mass yields on lixiviation with water, a solution of sodic telluride, which on exposure to the air, deposits tellurium as a gray powder. The pulverulent tellurium may be fused into a coherent mass under sodic chloride.

Properties.—Tellurium is a silver-white crystalline substance with a metallic lustre. At a high temperature it may be distilled. It dissolves in fuming sulphuric acid with a deep red color.

Reaction.—When heated in air it burns with a blue flame, forming tellurous anhydride, $\mathbf{Te}O_2$.

COMPOUNDS OF TELLURIUM WITH HYDROGEN, CHLORINE, AND OXYGEN.

TELLURETTED HYDROGEN.

$\mathbf{Te}H_2$.

Molecular weight = 127. *Molecular volume* $\square\square$. 1 *litre weighs* 63.5 *criths.*

Preparation.—Telluretted hydrogen is obtained by the action of dilute hydrochloric acid on ferrous or zincic telluride:

$$\begin{array}{ccccccc} \mathbf{Zn}\mathrm{Te}'' & + & 2\mathrm{HCl} & = & \mathbf{Te}\mathrm{H}_2 & + & \mathbf{Zn}\mathrm{Cl}_2. \\ \text{Zincic telluride.} & & \text{Hydrochloric acid.} & & \text{Telluretted hydrogen.} & & \text{Zincic chloride.} \end{array}$$

Properties.—Telluretted hydrogen is a colorless gas of a fetid odor, resembling that of sulphuretted hydrogen. It exhibits the same anomalies of dissociation as seleniuretted hydrogen. It may be ignited in air, and burns with a blue flame, forming tellurous anhydride and water:

$$\begin{array}{ccccccc} \mathbf{Te}\mathrm{H}_2 & + & 3\mathrm{O} & = & \mathbf{Te}\mathrm{O}_2 & + & \mathrm{OH}_2. \\ \text{Telluretted hydrogen.} & & & & \text{Tellurous anhydride.} & & \text{Water.} \end{array}$$

There are two chlorides of tellurium, $'\mathbf{Te}'_2Cl_2$ and $\mathbf{Te}Cl_4$.

Tellurous Anhydride, $\mathbf{Te}O_2$.—This compound is prepared like selenious anhydride (p 286), which it closely resembles in properties.

Tellurous Acid.—$\mathbf{Te}OHo_2$.—This acid is obtained as a white flocculent precipitate, when a solution of tellurium in dilute nitric acid is poured into water. It is decomposed at a temperature of 40° C. (104° F.) into anhydride and water. It dissolves more readily in hydrochloric acid than in water. Sulphurous acid precipitates tellurium from the solution (see *Selenious Acid*, p. 286).

Tellurous acid is a dibasic acid, forming acid and normal salts. Thus:

Hydric potassic tellurite, ... $\mathbf{Te}OHoKo$.
Normal potassic tellurite, ... $\mathbf{Te}OKo_2$.

Tetratellurites, produced by the combination of the normal tellurites with tellurous anhydride, are also known:

Dipotassic tetratellurite, ... $K{-}O{-}\overset{\overset{\displaystyle O}{\|}}{Te}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{Te}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{Te}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{Te}{-}O{-}K.$

Telluric Anhydride, $\mathbf{Te}O_3$.—Telluric anhydride is prepared by carefully heating telluric acid. It forms an orange-yellow mass. When strongly heated it is decomposed into tellurous anhydride and oxygen. It is insoluble in water. Boiling concentrated hydrochloric acid dissolves it slowly, converting it, with evolution of chlorine, into tellurous anhydride:

$$\underset{\substack{\text{Telluric}\\\text{anhydride.}}}{\mathbf{Te}O_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Tellurous}\\\text{anhydride.}}}{\mathbf{Te}O_2} + \underset{\text{Water.}}{\mathbf{O}H_2} + Cl_2.$$

Telluric Acid, $\mathbf{Te}O_2Ho_2$.—In order to prepare this compound tellurium is fused with a mixture of caustic potash and potassic chlorate. The tellurium is oxidized at the expense of the oxygen of the potassic chlorate to telluric anhydride, which combines with the alkaline base to form potassic tellurate:

$$Te + \underset{\substack{\text{Potassic}\\\text{chlorate.}}}{\left\{\begin{matrix}\mathbf{O}Cl\\\mathbf{O}Ko\end{matrix}\right.} = \underset{\substack{\text{Telluric}\\\text{anhydride.}}}{\mathbf{Te}O_3} + \underset{\substack{\text{Potassic}\\\text{chloride.}}}{KCl.}$$

$$\underset{\substack{\text{Telluric}\\\text{anhydride.}}}{\mathbf{Te}O_3} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{2KHo} = \underset{\substack{\text{Potassic}\\\text{tellurate.}}}{\mathbf{Te}O_2Ko_2} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

The fused mass is dissolved in water, and a solution of baric chloride is added, when insoluble baric tellurate is precipitated:

$$\underset{\substack{\text{Potassic}\\\text{tellurate.}}}{\mathbf{Te}O_2Ko_2} + \underset{\substack{\text{Baric}\\\text{chloride.}}}{\mathbf{Ba}Cl_2} = \underset{\substack{\text{Baric}\\\text{tellurate.}}}{\mathbf{Te}O_2Bao''} + \underset{\substack{\text{Potassic}\\\text{chloride.}}}{2KCl.}$$

The baric tellurate is suspended in water, and decomposed with the exact quantity of sulphuric acid. In this way insoluble baric sulphate and free telluric acid are formed. On evaporating the filtered solution, large colorless monoclinic crystals of hexabasic telluric acid, $\mathbf{Te}Ho_6$, are deposited. On heating to 160° these crystals part with two molecules of water, yielding dibasic telluric acid, $\mathbf{Te}O_2Ho_2$, as a white amorphous mass.

Telluric acid forms a series of somewhat complex salts. Among the potassium salts, for example, tellurates, ditellurates, and tetratellurates are known.

Tetrahydric dipotassic tellurate, . . . $TeHo_4Ko_2,3OH_2$.

Octohydric dipotassic ditellurate, . . $\left\{\begin{array}{l} TeHo_4Ko \\ O \\ TeHo_4Ko \end{array}\right.$.

Octohydric dipotassic tetratellurate, . $\left\{\begin{array}{l} TeHo_4Ko \\ O \\ TeO_2 \\ O \\ TeO_2 \\ O \\ TeHo_4Ko \end{array}\right.$.

CHAPTER XXVIII.

MONAD ELEMENTS.

SECTION II. (*Continued from* Chapter XXII.)

BROMINE, Br_2.

Atomic weight = 80. *Molecular weight* = 160. *Molecular volume* $\square\square$. 1 *litre of bromine vapor weighs* 80 *criths*. *Sp. gr.* 3.187. *Fuses at* —24.5° C. (—12.1° F.). *Boils at* 63° C. (145.4° F.). *Atomicity* $'$. *Evidence of atomicity:*

Hydrobromic acid, ...	HBr.
Potassic bromide, ...	KBr.
Argentic bromide, ...	$AgBr$.

History.—Bromine (from βρῶμος, a stench) was discovered in 1826, by Balard, in the mother-liquors obtained in the crystallization of common salt from sea-water.

Occurrence.—Bromine does not occur in the free state in nature. It is found in combination with metals as bromides, sodic bromide being the most common. This salt occurs in small quantity in sea-water, particularly in the water of the Dead Sea, and in greater abundance in many salt springs and deposits of rock salt. The salt mines of Stassfurt furnish 20,000 kilos. of bromine yearly.

Preparation.—1. The mother-liquors of saline waters containing bromides are treated with chlorine as long as the color of the liquid continues to become darker. In this way bromine is liberated, and may be distilled off and collected in a cooled receiver:

$$\underset{\text{Sodic bromide.}}{2NaBr} + Cl_2 = \underset{\text{Sodic chloride.}}{2NaCl} + Br_2.$$

An excess of chlorine must be avoided, as this would occasion the formation of a chloride of bromine.

On a large scale the mother liquors are mixed with an excess of sulphuric or hydrochloric acid, and a quantity of manganic peroxide exactly sufficient to liberate the bromine present (see Equation, *Preparation* 2) is added. As long as an excess of the peroxide is avoided, there is no danger of obtaining a product contaminated with chlorine, since any chlorine which might be liberated would at once set free its equivalent of bromine.

2. Bromine may also be obtained from pure bromides, in a reaction similar to that employed in the preparation of chlorine, by heating them with sulphuric acid and manganic peroxide:

$$\underset{\text{Sodic bromide.}}{2NaBr} + \underset{\text{Manganic peroxide.}}{\mathbf{Mn}O_2} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2} = Br_2 +$$

$$\underset{\text{Sodic sulphate.}}{\mathbf{S}O_2Nao_2} + \underset{\text{Manganous sulphate.}}{\mathbf{S}O_2Mno''} + \underset{\text{Water.}}{2\mathbf{O}H_2}$$

Properties.—Bromine is a heavy reddish-brown liquid, transparent only in thin layers. Its vapor possesses a considerable tension at ordinary temperatures. If a few drops be poured into a flask, the latter will be speedily filled with the reddish-brown vapor. At a temperature of —24.5° C. (—12.1° F.) bromine solidifies to a crystalline mass with a slight metallic lustre. Bromine has a powerful and unpleasant odor, resembling that of chlorine. Its vapor attacks the eyes and the organs of respiration. It is an irritant poison. When brought in contact with the skin, it produces dangerous wounds.

Throughout a considerable range of temperature above its boiling point, bromine has a vapor-density corresponding with the molecular formula Br_2. At higher temperatures the vapor-density diminishes, owing to a partial dissociation of the molecules of the vapor into single atoms. This dissociation, which occurs more readily than in the case of chlorine, but less readily than in the case of iodine, is not complete at 1600° C. (2912° F.), the highest temperature that has been employed in such determinations.

Bromine is soluble in about thirty times its weight of water at ordinary temperatures, the solubility decreasing as the temperature rises. The solution is of a reddish color, and, when exposed to a temperature of 0° C. deposits crystals of a hydrate, $Br_2,10\mathbf{O}H_2$, melting at 15° C. (59° F.). Bromine is more soluble in ether and carbonic disulphide than in water, and when an aqueous solution is agitated with either of these solvents, the bromine is extracted from the water and passes into the new solvent, which separates from the water as a dark-colored layer, on allowing the liquid to stand.

Moist bromine bleaches vegetable colors, but less powerfully than chlorine.

Bromine combines directly with many of the metals to form bromides. Antimony and tin inflame spontaneously in the vapor, and burn with great brilliancy. Potassium and bromine, when brought together at ordinary temperatures, unite, frequently with explosion;

but sodium must be heated to 200° C. in contact with bromine vapor, before any action occurs.

HYDROBROMIC ACID.

HBr.

Molecular weight = 81. *Molecular volume* $\square\square$. 1 *litre of hydrobromic acid weighs* 40.5 *criths. Fuses at* —73° C. (—99.4° F.). *Boils at* —69° C. (—92.2° F.).

Preparation.—1. When a mixture of hydrogen and bromine vapor is passed through a red-hot tube, or when a mixture of hydrogen and bromine vapor is burned in air, hydrobromic acid is formed by the direct combination of its elements:

$$H_2 + Br_2 = \underset{\text{Hydrobromic acid.}}{2HBr.}$$

2. It may be obtained by heating potassic bromide with phosphoric acid:

$$\underset{\substack{\text{Potassic}\\\text{bromide.}}}{3KBr} + \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{POHo_3} = \underset{\substack{\text{Potassic}\\\text{phosphate.}}}{POKo_3} + \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{3HBr.}$$

Sulphuric acid cannot be substituted for phosphoric acid in this reaction, as a portion of the hydrobromic acid is then decomposed, with liberation of bromine:

$$\underset{\substack{\text{Sulphuric}\\\text{acid.}}}{SO_2Ho_2} + \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{2HBr} = Br_2 + \underset{\text{Water.}}{2OH_2} + \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{SO_2.}$$

3. It is formed by the action of water upon phosphorous tribromide or phosphoric pentabromide:

$$\underset{\substack{\text{Phosphorous}\\\text{tribromide.}}}{P'''Br_3} + \underset{\text{Water.}}{3OH_2} = \underset{\substack{\text{Phosphorous}\\\text{acid.}}}{PoH_3} + \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{3HBr.}$$

$$\underset{\substack{\text{Phosphoric}\\\text{pentabromide.}}}{PBr_5} + \underset{\text{Water.}}{4OH_2} = \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{POHo_3} + \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{5HBr.}$$

These reactions may be most conveniently applied by gradually dropping the requisite quantity of bromine into water containing amorphous phosphorus. The bromides of phosphorus are decomposed at the moment of their formation:

$$P + Br_5 + \underset{\text{Water.}}{4OH_2} = \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{POHo_3} + \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{5HBr.}$$

This is the method most usually employed in the laboratory for the preparation of hydrobromic acid.

4. It may also be obtained in aqueous solution by passing sulphuretted hydrogen through water containing bromine:

$$\underset{\text{Sulphuretted hydrogen.}}{SH_2} + Br_2 = \underset{\text{Hydrobromic acid.}}{2HBr} + S.$$

Properties.—Hydrobromic acid is a colorless gas, with a pungent odor. It fumes strongly in contact with moist air. By means of pressure and cold it may be liquefied, and when cooled to —73° C. (—99.4° F.) solidifies to a colorless crystalline mass. Water absorbs more than its own weight of the gas, yielding a powerfully acid liquid. When a solution, saturated at a low temperature, is subjected to distillation, the liquid in the retort gradually becomes weaker, until it contains 48 per cent. of hydrobromic acid, when it distils unchanged between 125° and 126° C. (257°–259° F.), and possesses a specific gravity of 1.49 at 14° C. (57° F.). When an acid containing less than 48 per cent. is distilled, the liquid in the retort gradually becomes more concentrated till the above percentage is attained. This aqueous solution does not correspond with any definite hydrate, and its composition may be altered by altering the pressure under which the distillation takes place.

Reactions.—1. Chlorine decomposes the acid with liberation of bromine:

$$\underset{\text{Hydrobromic acid.}}{2HBr} + Cl_2 = \underset{\text{Hydrochloric acid.}}{2HCl} + Br_2.$$

2. By the action of atmospheric oxygen a small quantity of bromine is liberated from hydrobromic acid in aqueous solution, but the decomposition is soon arrested:

$$\underset{\text{Hydrobromic acid.}}{4HBr} + O_2 = \underset{\text{Water.}}{2OH_2} + 2Br_2.$$

3. In contact with metallic oxides and hydrates bromides are formed. Argentic bromide, AgBr, and mercurous bromide, $'Hg'_2Br_2$, are insoluble in water; plumbic bromide, $PbBr_2$, is sparingly soluble; all the other bromides dissolve readily.

COMPOUNDS OF BROMINE WITH OXYGEN AND HYDROXYL.

Hypobromous acid, ... OBrH.

Bromic acid, ... $\begin{cases} OBr \\ O \\ OH \end{cases}$.

The graphic formulæ of these compounds are analogous to those of the corresponding chlorine compounds, given on page 177.

HYPOBROMOUS ACID.

$OBrH$.

Preparation.—An aqueous solution of this very unstable compound may be obtained by agitating mercuric oxide with bromine-water:

$$\underset{\text{Mercuric oxide.}}{2HgO} + \underset{\text{Water.}}{OH_2} + 2Br_2 = \underset{\text{Hypobromous acid.}}{2OBrH} + \underset{\text{Mercuric oxybromide.}}{\left\{\begin{matrix} HgBr \\ O \\ HgBr \end{matrix}\right.}.$$

The corresponding anhydride, OBr_2, has not been prepared.

BROMIC ACID.

$$\left\{\begin{matrix} OBr \\ OHo \end{matrix}\right.$$

Preparation.—Bromic acid is best prepared by decomposing a solution of baric bromate with the requisite quantity of sulphuric acid:

$$\underset{\text{Baric bromate.}}{\left\{\begin{matrix} OBr \\ O \\ Bao'' \\ O \\ OBr \end{matrix}\right.} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Bromic acid.}}{2\left\{\begin{matrix} OBr \\ OHo \end{matrix}\right.} + \underset{\text{Baric sulphate.}}{SO_2Bao''}.$$

The aqueous solution may be concentrated *in vacuo* till it contains 1 molecule of acid to 7 of water. Beyond this point it is decomposed into water, bromine, and oxygen. The same decomposition takes place when the dilute solution is boiled:

$$\underset{\text{Bromic acid.}}{4\left\{\begin{matrix} OBr \\ OHo \end{matrix}\right.} = 2Br_2 + \underset{\text{Water.}}{2OH_2} + 5O_2.$$

Bromic acid closely resembles chloric acid in its properties.

Preparation of Bromates.—1. When bromine is added to a solution of a metallic hydrate, a mixture of bromate and bromide is formed:

$$\underset{\text{Potassic hydrate.}}{6KHo} + 3Br_2 = \underset{\text{Potassic bromide.}}{5KBr} + \underset{\text{Potassic bromate.}}{\left\{\begin{matrix} OBr \\ OKo \end{matrix}\right.} + \underset{\text{Water.}}{3OH_2}.$$

The potassic bromate is much less soluble than the bromide, and may be separated from it by crystallization.

2. Potassic bromate is also formed when bromine is added to a solution of potassic hydrate or carbonate, and chlorine is passed into the liquid:

$$\underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{6KHo} + Br + 5Cl = \underset{\substack{\text{Potassic}\\ \text{chloride.}}}{5KCl} + \underset{\substack{\text{Potassic}\\ \text{bromate.}}}{\left\{\begin{matrix} \mathbf{O}Br \\ \mathbf{O}Ko \end{matrix}\right.} + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

In this way the whole of the bromine is converted into bromate.

Character of the Bromates.—Some of the bromates, when heated, lose oxygen, and are transformed into bromides:

$$\underset{\substack{\text{Potassic}\\ \text{bromate.}}}{2\left\{\begin{matrix} \mathbf{O}Br \\ \mathbf{O}Ko \end{matrix}\right.} = \underset{\substack{\text{Potassic}\\ \text{bromide.}}}{2KBr} + 3O_2.$$

Others evolve bromine and a portion of their oxygen, leaving metallic oxides:

$$\underset{\substack{\text{Magnesic}\\ \text{bromate.}}}{2\left\{\begin{matrix} \mathbf{O}Br \\ O \\ Mgo'' \\ O \\ \mathbf{O}Br \end{matrix}\right.} = \underset{\substack{\text{Magnesic}\\ \text{oxide.}}}{2MgO} + 2Br_2 + 5O_2.$$

IODINE, I_2.

Atomic weight = 127. *Molecular weight* = 254. *Molecular volume* $\square\square$. 1 *litre of iodine vapor weighs* 127 *criths*. *Sp. gr.* 4.95. *Fuses at* 114° C. (237° F.). *Boils above* 200° C. (392° F.). *Atomicity* '.* *Evidence of atomicity:*

Hydriodic acid, ...	HI.
Potassic iodide, ...	KI.
Argentic iodide, ...	AgI.

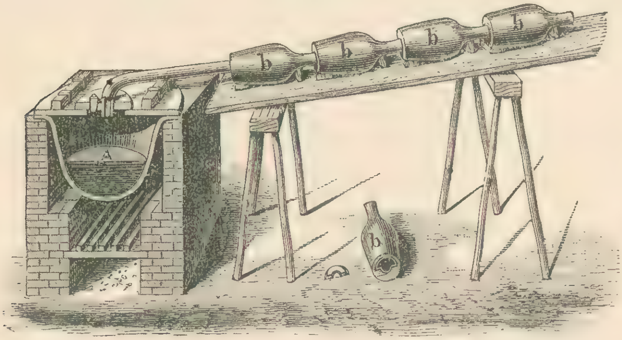
History.—Iodine was discovered in 1812 by Courtois in the mother-liquors of soda prepared from the ashes of sea-weed. The first thorough investigation of its properties is due to Gay-Lussac.

Occurrence.—Iodine is always found in combination with metals, generally associated with chlorine. In this form it occurs in small quantities in some mineral springs and in sea-water, from which last it is absorbed in larger quantity by various kinds of sea-weed. From these the iodine of commerce is obtained. It has also been detected in some marine animals, such as sponges and oysters. The iodides of silver and lead occur as rare minerals.

* See, however, Periodates.

Manufacture.—Sea-weed is burned in pits, the temperature being kept as low as possible in order to prevent loss from volatilization of the salts of iodine. The ash thus obtained is known as *kelp*. The soluble salts, consisting of alkaline carbonates, sulphates, chlorides, bromides, and iodides, are extracted from the ash with water. The solution is evaporated, and the carbonates, sulphates, and chlorides are removed by crystallization. To the mother-liquor, containing the

Fig. 43.



bromides and iodides, sulphuric acid is added, which causes a separation of sulphur, owing to the presence of sulphides and sulphites. The sulphur and crystals of sulphate are removed, and the liquid is transferred to a large iron retort A (Fig. 43), lined with lead. Heat is applied and manganic peroxide is added in small portions at a time. Iodine is thus liberated according to the equation:

$$\underset{\substack{\text{Sodic}\\ \text{iodide.}}}{2NaI} + \underset{\substack{\text{Manganic}\\ \text{oxide.}}}{\mathbf{MnO_2}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{2\mathbf{SO_2}Ho_2} = \underset{\substack{\text{Sodic}\\ \text{sulphate.}}}{\mathbf{SO_2}Nao_2}$$

$$+ \underset{\text{Manganous sulphate.}}{\mathbf{SO_2}Mno''} + I_2 + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

and, distilling over, is condensed in a series of stoneware receivers, *b b b*, fitting one into the other as in the figure.

When the iodine ceases to distil over, the receiver is changed, and more manganic peroxide is added. This liberates the bromine, which, on account of its superior affinity for hydrogen and bases, is given off later than the iodine (see equation, p. 297). The bromine is distilled off and collected.

Sometimes the dried sea-weed is carbonized in retorts and the resulting charcoal lixiviated with water. In this way the loss of iodine by volatilization is avoided; but, on the other hand, it is found impossible to extract the whole of the iodine salts from the charcoal.

Properties.—Iodine forms bluish-black tabular rhombic crystals, with a metallic lustre. It possesses a peculiar and irritating odor, distantly resembling that of chlorine. When heated, it gives off a vapor

of a magnificent violet color (hence the name of this element, from ἰοειδής, violet-colored). At higher temperatures and when free from admixture of air, this vapor assumes a deep blue tint. The vapor possesses a characteristic absorption-spectrum.

The vapor-density of iodine at temperatures up to 700° C. (1292° F.) corresponds with the molecular formula I_2. Above this temperature the vapor-density diminishes as the temperature rises, till at 1400° C. (25.52° F.) it is somewhat less than two-thirds of the vapor-density below 700° C. This diminution is due to a partial dissociation of the molecules of iodine into free atoms. If the iodine vapor be mixed with four-fifths of its volume of air, in order to reduce the pressure of the iodine vapor and thus increase the dissociation, the vapor-density of the iodine at 1400° C. is only half as great as at 700° C.; that is to say, the vapor-density corresponds with the molecular formula I, and the iodine vapor at that temperature is mon-atomic. At temperatures above 1400° C. no further diminution occurs under these circumstances.

Iodine is very slightly soluble in water, but dissolves readily in presence of hydriodic acid or of soluble iodides. Alcohol dissolves it more freely, whilst in ether, chloroform, and carbonic disulphide, it is very readily soluble. The aqueous, ethereal, and alcoholic solutions are brown; those in chloroform and carbonic disulphide are violet.

The smallest trace of free iodine imparts to starch paste a splendid blue color, which disappears on heating, but returns, although with diminished intensity, on subsequent cooling.

Reactions.—1. Iodine is expelled by chlorine and bromine from all its compounds with electro-positive elements:

$$\underset{\text{Potassic iodide.}}{2KI} + Cl_2 = \underset{\text{Potassic chloride.}}{2KCl} + I_2.$$

$$\underset{\text{Potassic iodide.}}{2KI} + Br_2 = \underset{\text{Potassic bromide.}}{2KBr} + I_2.$$

2. With a solution of calcic hydrate, iodine yields a liquid which bleaches in alkaline solution, and therefore probably contains *calcic iodohypiodite:*

$$\underset{\text{Calcic hydrate.}}{\mathbf{Ca}Ho_2} + I_2 = \underset{\substack{\text{Calcic}\\\text{iodohypiodite.}}}{\mathbf{Ca}(OI)I} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

The bleaching power diminishes gradually on standing, and more rapidly on boiling or by exposure to light. When the bleaching property has disappeared, the solution contains only a mixture of calcic iodate and calcic iodide.

3. Iodine unites directly with metals and non-metals, the process of combination being frequently accompanied with evolution of heat and light. Phosphorus ignites when brought into contact with solid iodine, and powdered antimony, when thrown into iodine vapor, bursts into flame.

HYDRIODIC ACID.

HI.

Molecular weight = 128. *Molecular volume* $\square\!\square$. 1 *litre of hydriodic acid weighs* 64 *criths. Fuses at* —55° C. (—67° F.).

Preparation.—1. Hydriodic acid is formed by the direct union of its elements when a mixture of iodine vapor and hydrogen is passed through a red-hot tube or over spongy platinum gently heated:

$$H_2 + I_2 = 2HI.$$

2. It is formed when an iodide is heated with phosphoric acid:

$$\underset{\substack{\text{Potassic}\\\text{iodide.}}}{3KI} + \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{POHo_3} = \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{3HI} + \underset{\substack{\text{Potassic}\\\text{phosphate.}}}{POKo_3}.$$

Sulphuric acid cannot be substituted for phosphoric acid in this reaction, as it liberates iodine from hydriodic acid:

$$\underset{\substack{\text{Hydriodic}\\\text{acid.}}}{2HI} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{SO_2Ho_2} = I_2 + \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{SO_2} + \underset{\text{Water.}}{2OH_2}.$$

An aqueous solution of hyriodic acid may however be prepared by decomposing a solution of baric iodide with the exact quantity of dilute sulphuric acid, the sulphuric acid being in this case immediately withdrawn from the reaction in the form of insoluble baric sulphate.

3. It is also formed by decomposing phosphorous triiodide by water:

$$\underset{\substack{\text{Phosphorous}\\\text{triiodide.}}}{PI_3} + \underset{\text{Water.}}{3OH_2} = \underset{\substack{\text{Phosphorous}\\\text{acid.}}}{PHo_3} + \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{3HI}.$$

4. It may be prepared by heating together water, potassic iodide, iodine, and amorphous phosphorus:

$$\underset{\substack{\text{Potassic}\\\text{iodide.}}}{4KI} + P_2 + 5I_2 + \underset{\text{Water.}}{8OH_2} = \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{14HI} + \underset{\substack{\text{Hydric dipotassic}\\\text{phosphate.}}}{2POHoKo_2}.$$

An aqueous solution of hydriodic acid prepared by Method 5 (see below) may be advantageously substituted for the solution of potassic iodide in the above reaction. The amorphous phosphorus is placed in a retort with the neck sloped slightly upwards, and a solution of 2 parts of iodine in 1 part of aqueous hydriodic acid (b. p. 127°) is allowed to drop gradually through the tubulure from a stoppered funnel. Gaseous hydriodic acid is evolved in a steady stream. When the action begins to slacken, a gentle heat may be applied.

5. A solution of hydriodic acid may be readily obtained by passing sulphuretted hydrogen through water in which iodine is suspended:

$$\underset{\text{Sulphuretted hydrogen.}}{2SH_2} + 2I_2 = \underset{\text{Hydriodic acid.}}{4HI} + S_2.$$

As the reaction proceeds the unattacked iodine dissolves in the aqueous hydriodic acid and facilitates the decomposition.

Properties.—Hydriodic acid is a colorless gas, fuming in contact with moist air, and possessing a pungent odor. At a temperature of 0° C. and under a pressure of 4 atmospheres, it condenses to a colorless liquid which solidifies at —55° C. (—67° F.).

It is readily decomposed by heat. A hot glass rod plunged into a vessel filled with the gas, causes the immediate separation of violet vapors of iodine.

It is readily absorbed by water, forming a strongly acid liquid. A solution saturated at 0° C. has a sp. gr. of 2. Aqueous hydriodic acid behaves on distillation like hydrochloric and hydrobromic acids (*q.v.*). The strongest acid obtainable by distillation has a sp. gr. of 1.67, contains 57.7 per cent. of hydriodic acid, and boils at 127° C. (260.6° F.). When a weaker or a stronger acid is distilled, the composition of the distillate gradually becomes stronger or weaker until an acid of the above strength and boiling-point distils over unchanged. This acid does not correspond with any definite hydrate and, as in the case of hydrochloric and hydrobromic acids, the composition of the distillate may be made to vary by varying the pressure under which distillation takes place.

The aqueous solution when pure is colorless, but in contact with the oxygen of the air, it rapidly becomes brown from separation of iodine, which dissolves in the aqueous acid:

$$\underset{\text{Hydriodic acid.}}{4HI} + O_2 = \underset{\text{Water.}}{2OH_2} + 2I_2.$$

Oxidizing agents have a similar action. Owing to this property of readily parting with its hydrogen, hydriodic acid is frequently employed as a reducing agent, particularly at higher temperatures and in the case of organic substances.

Reactions.—1. Chlorine and bromine decompose hydriodic acid, liberating iodine:

$$\underset{\text{Hydriodic acid.}}{2HI} + Cl_2 = \underset{\text{Hydrochloric acid.}}{2HCl} + I_2.$$

2. Mercury rapidly decomposes it, with liberation of hydrogen:

$$\underset{\text{Hydriodic acid.}}{2HI} + 2Hg = \underset{\text{Mercurous iodide.}}{'Hg'_2I_2} + H_2.$$

3. With metallic oxides, hydrates, and some salts, it forms iodides.

Even argentic chloride is transformed by hydriodic acid into argentic iodide:

$AgCl$	+	HI	=	AgI	+	HCl.
Argentic chloride.		Hydriodic acid.		Argentic iodide.		Hydrochloric acid.

Iodides.—The iodides closely resemble the chlorides and bromides. Argentic iodide, AgI, mercurous iodide, $'\mathbf{Hg}'_2I_2$, mercuric iodide, $\mathbf{Hg}I_2$, and cuprous iodide, $'\mathbf{Cu}'_2I_2$, are insoluble in water; plumbic iodide, $\mathbf{Pb}I_2$, dissolves very slightly; the other iodides are readily soluble.

COMPOUNDS OF IODINE WITH CHLORINE.

Hypiodous chloride, ... ICl.
Iodous chloride, ... ICl_3.

These compounds are formed by the direct union of their elements.

HYPIODOUS CHLORIDE.

ICl.

Molecular weight = 162.5. *Fuses at* 24.7° C. (76.5° F.). *Boils at* 101° C. (213.8° F.).

Preparation.—This compound is obtained by passing dry chlorine over iodine, interrupting the operation as soon as the whole of the iodine has liquefied. The reddish-brown liquid thus obtained solidifies on standing.

Properties.—Hypiodous chloride forms large prismatic crystals of a hyacinth-red color.

Reaction.—Water decomposes it with formation of iodic acid, hydrochloric acid, and free iodine:

$5ICl$	+	$3\mathbf{O}H_2$	=	$\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Ho\end{matrix}\right.$	+	$5HCl$	+	$2I_2$.
Hypiodous chloride.		Water.		Iodic acid.		Hydrochloric acid.		

IODOUS CHLORIDE.

ICl_3.

Molecular weight = 233.5.

Preparation.—Iodous chloride is formed by the action of an excess of chlorine upon iodine or upon the foregoing compound.

Properties.—It forms long yellow crystals which sublime at ordinary temperatures. It fuses at 20°–25° C. (68°–77° F.), with dissociation into hypiodous chloride and free chlorine.

Reaction.—With water it is decomposed, yielding the same products as hypiodous chloride (see preceding compound):

$$\underset{\text{Iodous chloride.}}{5ICl_3} + \underset{\text{Water.}}{9OH_2} = \underset{\text{Iodic acid.}}{3\left\{\begin{matrix}OI\\OHo\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{15HCl} + I_2.$$

COMPOUNDS OF IODINE WITH OXYGEN AND HYDROXYL.

$$\text{Iodic anhydride, ...} \left\{\begin{matrix}OI\\O\\O\\O\\OI\end{matrix}\right. .$$

$$\text{Iodic acid, ...} \left\{\begin{matrix}OI\\OHo\end{matrix}\right. .$$

$$\text{Periodic acid, ...} \left\{\begin{matrix}OI\\O\\OHo\end{matrix}\right. .$$

The graphic formulæ of these compounds are analogous to those of the corresponding chlorine compounds given on p. 177.

IODIC ANHYDRIDE.

$$I_2O_5 \text{ or } \left\{\begin{matrix}OI\\O\\O\\O\\OI\end{matrix}\right. .$$

Preparation.—This compound is formed when iodic acid is heated to 170° C.:

$$\underset{\text{Iodic acid.}}{2\left\{\begin{matrix}OI\\OHo\end{matrix}\right.} = \underset{\text{Iodic anhydride.}}{\left\{\begin{matrix}OI\\O\\O\\O\\OI\end{matrix}\right.} + \underset{\text{Water.}}{OH_2}.$$

Properties.—Iodic anhydride is a white crystalline powder possessing a sp. gr. of 4.48.

Reactions.—1. When heated to 300° C. (572° F.) it is decomposed into iodine and oxygen.

2. Gaseous hydrochloric acid decomposes it with elevation of temperature, iodous trichloride and water being formed, and chlorine liberated:

$$\underset{\text{Iodic anhydride.}}{I_2O_5} + \underset{\text{Hydrochloric acid.}}{10HCl} = \underset{\text{Iodous trichloride.}}{2ICl_3} + \underset{\text{Water.}}{5OH_2} + 2Cl_2.$$

3. It dissolves in water, forming iodic acid.

IODIC ACID.

$$\left\{\begin{array}{l} OI \\ OHo \end{array}\right.$$

Preparation.—1. Iodic acid may be obtained by decomposing a solution of baric iodate with the equivalent quantity of sulphuric acid:

$$\underset{\text{Baric iodate.}}{\left\{\begin{array}{l} OI \\ O \\ Bao'' \\ O \\ OI \end{array}\right.} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Iodic acid.}}{2\left\{\begin{array}{l} OI \\ OHo \end{array}\right.} + \underset{\text{Baric sulphate.}}{SO_2Bao''}.$$

The aqueous solution of iodic acid may be evaporated at 100° C. without decomposition.

2. It is best prepared by oxidizing iodine with strong boiling nitric acid:

$$\underset{\text{Nitric acid.}}{6NO_2Ho} + I_2 = \underset{\text{Iodic acid.}}{2\left\{\begin{array}{l} OI \\ OHo \end{array}\right.} + \underset{\text{Water.}}{2OH_2} + \underset{\text{Nitrous anhydride.}}{2N_2O_3} + \underset{\text{Nitric peroxide.}}{'N^{iv}{}_2O_4}.$$

3. It is also formed when chlorine is passed into water in which finely powdered iodine is suspended:

$$I_2 + \underset{\text{Water.}}{6OH_2} + 5Cl_2 = \underset{\text{Iodic acid.}}{2\left\{\begin{array}{l} OI \\ OHo \end{array}\right.} + \underset{\text{Hydrochloric acid.}}{10HCl}.$$

Properties.—Iodic acid forms colorless rhombic crystals of sp. gr. 4.629. It is very soluble in water. At a temperature of 170° C. (338° F.) it gives off water, and is converted into anhydride.

Reactions.—1. In contact with hydriodic acid it forms water and iodine:

$$\underset{\text{Iodic acid.}}{\left\{\begin{array}{l} OI \\ OHo \end{array}\right.} + \underset{\text{Hydriodic acid.}}{5HI} = \underset{\text{Water.}}{3OH_2} + 3I_2.$$

2. It is reduced by many other deoxidizing agents:

$$\underset{\text{Iodic acid.}}{2\left\{\begin{matrix}OI\\OHo\end{matrix}\right.} + \underset{\text{Sulphuretted hydrogen.}}{5SH_2} = I_2 + 5S + \underset{\text{Water.}}{6OH_2}.$$

$$\underset{\text{Iodic acid.}}{2\left\{\begin{matrix}OI\\OHo\end{matrix}\right.} + \underset{\text{Sulphurous anhydride.}}{5SO_2} + \underset{\text{Water.}}{4OH_2} = I_2 + \underset{\text{Sulphuric acid.}}{5SO_2Ho_2}.$$

Preparation of Iodates.—Iodates may be obtained by the following methods:

1. By treating solutions of metallic hydrates with iodine, and separating the iodate by crystallization:

$$\underset{\text{Potassic hydrate.}}{6KHo} + 3I_2 = \underset{\text{Potassic iodide.}}{5KI} + \underset{\text{Potassic iodate.}}{\left\{\begin{matrix}OI\\OKo\end{matrix}\right.} + \underset{\text{Water.}}{3OH_2}.$$

2. By dissolving iodine in potassic hydrate and treating the mixture with chlorine:

$$\underset{\text{Potassic hydrate.}}{12KHo} + I_2 + 5Cl_2 = \underset{\text{Potassic chloride.}}{10KCl} + \underset{\text{Potassic iodate.}}{2\left\{\begin{matrix}OI\\OKo\end{matrix}\right.} + \underset{\text{Water.}}{6OH_2}.$$

In this way the whole of the iodine is converted into iodate.

3. By heating together potassic chlorate and iodine:

$$I_2 + \underset{\text{Potassic chlorate.}}{\left\{\begin{matrix}OCl\\OKo\end{matrix}\right.} = \underset{\text{Hypiodous chloride.}}{ICl} + \underset{\text{Potassic iodate.}}{\left\{\begin{matrix}OI\\OKo\end{matrix}\right.}.$$

Character of Iodates.—The iodates are nearly all insoluble in water; those of the alkalies are the most soluble.

Iodic acid, though a monobasic acid, forms hyper-acid salts. Thus in the case of potassium, the following salts are known:

Normal potassic iodate, ...	$\left\{\begin{matrix}OI\\OKo\end{matrix}\right.$.
Acid potassic iodate, ...	$\left\{\begin{matrix}OI\\OKo\end{matrix}\right.$, $\left\{\begin{matrix}OI\\OHo\end{matrix}\right.$.
Di-acid potassic iodate, ...	$\left\{\begin{matrix}OI\\OKo\end{matrix}\right.$, $2\left\{\begin{matrix}OI\\OHo\end{matrix}\right.$.

All the iodates are decomposed by heat. Some break up into iodides and oxygen, others into metallic oxides, iodine, and oxygen:

$$\left\{\begin{matrix}\mathrm{OI}\\ \mathrm{OKo}\end{matrix}\right. = \mathrm{KI} + 3\mathrm{O}.$$
$$\underset{\text{Potassic iodate.}}{} \qquad \underset{\text{Potassic iodide.}}{}$$

$$\left\{\begin{matrix}\mathrm{OI}\\ \mathrm{O}\\ \mathrm{Mgo''}\\ \mathrm{O}\\ \mathrm{OI}\end{matrix}\right. = \mathrm{MgO} + \mathrm{I_2} + 5\mathrm{O}.$$
$$\underset{\text{Magnesic iodate.}}{} \qquad \underset{\text{Magnesic oxide.}}{}$$

PERIODIC ACID.

$$\left\{\begin{matrix}\mathrm{OI}\\ \mathrm{O}\\ \mathrm{OHo}\end{matrix}\right. .$$

Preparation.—1. Periodic acid is obtained by decomposing plumbic periodate with sulphuric acid:

$$\left\{\begin{matrix}\mathrm{OI}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{Pbo''}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{OI}\end{matrix}\right. + \mathrm{SO_2Ho_2} = 2\left\{\begin{matrix}\mathrm{OI}\\ \mathrm{O}\\ \mathrm{OHo}\end{matrix}\right. + \mathrm{SO_2Pbo''}.$$
$$\underset{\text{Plumbic periodate.}}{} \qquad \underset{\text{Sulphuric acid.}}{} \qquad \underset{\text{Periodic acid.}}{} \qquad \underset{\text{Plumbic sulphate.}}{}$$

2. Argentic periodate is decomposed on boiling with water into an insoluble basic salt of the formula IO_5HAg_2,OH_2 and free periodic acid:

$$2\left\{\begin{matrix}\mathrm{OI}\\ \mathrm{O}\\ \mathrm{OAgo}\end{matrix}\right. + 2\mathrm{OH_2} = \mathrm{IO_5HAg_2,OH_2} + \left\{\begin{matrix}\mathrm{OI}\\ \mathrm{O}\\ \mathrm{OHo}\end{matrix}\right. .$$
$$\underset{\text{Argentic periodate.}}{} \qquad \underset{\text{Water.}}{} \qquad \underset{\text{Basic argentic periodate.}}{} \qquad \underset{\text{Periodic acid.}}{}$$

The periodic acid remains in solution and may be obtained on evaporation in crystals of the formula $\left\{\begin{matrix}\mathrm{OI}\\ \mathrm{O}\\ \mathrm{OHo}\end{matrix}\right. ,2\mathrm{OH_2}$.

3. It is also formed when iodine is added to an aqueous solution of perchloric acid:

$$2\left\{\begin{matrix}\mathrm{OCl}\\ \mathrm{O}\\ \mathrm{OHo}\end{matrix}\right. + \mathrm{I_2} = 2\left\{\begin{matrix}\mathrm{OI}\\ \mathrm{O}\\ \mathrm{OHo}\end{matrix}\right. + \mathrm{Cl_2}.$$
$$\underset{\text{Perchloric acid.}}{} \qquad \underset{\text{Periodic acid.}}{}$$

Properties.—Normal periodic acid, $\left\{\begin{array}{l}\mathbf{O}\mathrm{I}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Ho}\end{array}\right.$, has not been obtained. The crystals which are formed when an aqueous solution of the acid is evaporated, contain two molecules of water of crystallization, which they retain at 100° C. They fuse between 130° and 136° C. (266°–277° F.), and are slowly converted into iodic anhydride, oxygen, and water. At 200° C. (392° F.) this change takes place rapidly.

Preparation of Periodates.—1. Sodic periodate may be prepared by passing chlorine through mixed solutions of sodic hydrate and sodic iodate:

$$\underset{\text{Sodic iodate.}}{\left\{\begin{array}{l}\mathbf{O}\mathrm{I}\\ \mathbf{O}\mathrm{Nao}\end{array}\right.} + \underset{\text{Sodic hydrate.}}{2\mathrm{NaHo}} + \mathrm{Cl}_2 = \underset{\text{Sodic periodate.}}{\left\{\begin{array}{l}\mathbf{O}\mathrm{I}\\ \mathrm{O}\\ \mathbf{O}\mathrm{Nao}\end{array}\right.} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2} + \underset{\text{Sodic chloride.}}{2\mathrm{NaCl}}.$$

2. A basic baric periodate may be obtained by heating baric iodate:

$$\underset{\text{Baric iodate.}}{5\left\{\begin{array}{l}\mathbf{O}\mathrm{I}\\ \mathrm{O}\\ \mathrm{Bao}''\\ \mathrm{O}\\ \mathbf{O}\mathrm{I}\end{array}\right.} = \underset{\text{Basic baric periodate.}}{\left\{\begin{array}{l}\mathbf{O}\mathrm{I}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{Bao}'',4\mathbf{Ba}\mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathbf{O}\mathrm{I}\end{array}\right.} + 4\mathrm{I}_2 + 9\mathrm{O}_2.$$

This basic baric periodate is not decomposed at a red heat, whereas the other periodates part with their oxygen at this temperature.

Character of the Periodates. Atomicity of Iodine.—Periodic acid forms a series of remarkably complex salts, the classification of which is attended with some difficulty. Their constitution may, however, be readily explained on the supposition that, in this acid, iodine possesses the character of a heptad. Of course this would involve the assumption that iodine is pentadic in iodic acid, and triadic in iodous trichloride, whilst an extension of these atomicities to chlorine and bromine would be unavoidable. As, however, in these elements the monadic character is by far the most prominent, it has been thought advisable to adhere for the present to this classification. Future investigation may establish their polyadic character. In this connection it is worthy of note that electronegative elements exhibit as a rule a more polyadic character in their combinations with oxygen than in their combinations with hydrogen and metals.

The following table contains a list of the periodic acids and their salts, formulated both with heptadic and with monadic iodine, showing the greater simplicity resulting from the former method. The names of periodic acids which are known only in the form of their salts, are inclosed within brackets:

Name of compound.	With I^{vii}.	With I'.
(Monobasic periodic acid)	IO_3Ho	$^{iv}O''_3IHo$
(Tribasic periodic acid)	IO_2Ho_3	$^{iv}O''_3IHo,OH_2$
Pentabasic periodic acid	$IOHo_5$	$^{iv}O''_3IHo,2OH_2$
(Tetrabasic anhydroperiodic acid)	$\left\{\begin{matrix}IO_2Ho_2\\O\\IO_2Ho_2\end{matrix}\right.$	$2^{iv}O''_3IHo,OH_2$
(Octobasic anhydroperiodic acid)	$\left\{\begin{matrix}IOHo_4\\O\\IOHo_4\end{matrix}\right.$	$2^{iv}O''_3IHo,3OH_2$
Potassic periodate	IO_3Ko	$^{iv}O''_3IKo$
Triargentic periodate	IO_2Ago_3	$^{iv}O''_3IAgo,OAg_2$
Triplumbic periodate	$\begin{matrix}IO_2\\IO_2\end{matrix}Pbo''_3$	$\begin{matrix}^{iv}O''_3I\\^{iv}O''_3I\end{matrix}Pbo'',2PbO$
Pentargentic periodate	$IOAgo_5$	$^{iv}O''_3IAgo,2OAg_2$
Trihydric diargentic periodate	$IOHo_3Ago_2$	$2^{iv}O''_3IAgo,OAg_2,3OH_2$
Pentabaric periodate	$\begin{matrix}IO\\IO\end{matrix}Bao''_5$	$\begin{matrix}^{iv}O''_3I\\^{iv}O''_3I\end{matrix}Bao'',4BaO$
Tetrargentic anhydroperiodate	$\left\{\begin{matrix}IO_2Ago_2\\O\\IO_2Ago_2\end{matrix}\right.$	$2^{iv}O''_3IAgo,OAg_2$
Tetrazincic anhydroperiodate	$\left\{\begin{matrix}IOZno''_2\\O\\IOZno''_2\end{matrix}\right.$	$\begin{matrix}^{iv}O''_3I\\^{iv}O''_3I\end{matrix}Zno'',3ZnO$

The periodates are, as a rule, only sparingly soluble in water.

FLUORINE, F_2?

Atomic weight = 19. *Molecular weight* = 38 (?). *Atomicity* $'$. *Evidence of atomicity:*

Hydrofluoric acid, ... HF.

Occurrence.—Fluorine occurs in nature in combination with metals as fluorides. The most common of these is calcic fluoride or fluorspar, CaF_2, known also as the Derbyshire spar. Cryolite, a mineral occurring in Greenland, is a double fluoride of sodium and aluminium, possessing the formula $'Al'''_2F_6,6NaF$. Fluorine also occurs in small quantity in various other minerals, such as apatite, topaz, etc. In the animal kingdom it has been found in minute traces in the enamel of the teeth and in the bones.

Attempts to isolate Fluorine.—Little is known of fluorine in the free state. So great is the affinity of this element that as soon as it is expelled from one combination it enters into another. Its isolation has from time to time been announced, but a repetition of the experiments by other investigators has, till lately, failed to confirm the supposed results. Argentic fluoride is decomposed at a red heat by chlorine, bromine, or iodine, with formation of a chloride, bromide, or iodide of silver; but the liberated fluorine instantly combines with the material of which the vessels employed in the experiment are composed. Vessels of glass, silver, gold, platinum, and graphite have been tried, but

without success. In like manner in the electrolysis of fused fluorides, the fluorine combines with the material of the positive electrode.

The attempt to employ vessels of fluorspar in the above decompositions has proved unsuccessful.

Latterly, however, Brauner, in heating ceric tetrafluoride, has found that it is converted into diceric hexafluoride, whilst a gas is evolved which smells like chlorine, and liberates iodine from potassic iodide. The reaction probably occurs according to the equation :

$$\underset{\text{Ceric tetrafluoride.}}{2\mathbf{Ce}F_4} = \underset{\text{Diceric hexafluoride.}}{'\mathbf{Ce}'''_2F_6} + F_2.$$

COMPOUND OF FLUORINE WITH HYDROGEN.

HYDROFLUORIC ACID.

HF.

Molecular weight = 20.* *Molecular volume* $\square\square$. 1 *litre weighs* 10 *criths.* *Boils at* 19.4° C. (66.9° F.). *Sp. gr. of liquid* 0.9875 *at* 13° C. (55° F.).

Preparation.—1. Hydrofluoric acid may be obtained by heating calcic fluoride or cryolite with concentrated sulphuric acid in a leaden or platinum retort (Fig. 44), which is connected with a **U**-tube of the same metal :

$$\underset{\text{Calcic fluoride.}}{\mathbf{Ca}F_2} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} = \underset{\text{Hydrofluoric acid.}}{2HF} + \underset{\text{Calcic sulphate.}}{\mathbf{S}O_2Cao''}.$$

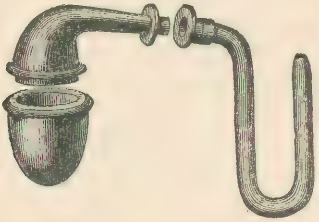
A very concentrated acid distils over and condenses in the **U**-tube, which is cooled by a freezing mixture. If an aqueous solution is required, the acid may be passed at once into water.

2. In order to obtain a perfectly anhydrous acid, the double fluoride of hydrogen and potassium (HF,KF), which must be previously fused in order to free it from the last traces of moisture, is heated in a platinum retort. The condenser and receiver must also be of platinum. The anhydrous hydrofluoric acid distils over, whilst potassic fluoride remains behind in the retort. The condensation is effected by means of

* Kletzinsky has found that hydrofluoric acid at a temperature just above its boiling-point possesses a vapor-density corresponding with the molecular weight 40, and therefore with the molecular formula H_2F_2. Mallet, experimenting at a temperature of 25° C. (77° F.), arrived at the same result. The vapor-density at these temperatures is twice as great as at 100° C., at which temperature it corresponds as above with the formula HF. The existence of such a molecule as H_2F_2 could best be accounted for on the supposition that fluorine is a triad in this compound, thus: H—F=F—H. This view finds further support in the existence of a *hydric potassic fluoride*, which would thus be formulated: H—F=F—K. The greater molecular weight of hydrofluoric acid at lower temperatures accounts also for the relatively high boiling-point of this acid as compared with the other hydracids.

a freezing mixture, and great care is required in performing the operation, owing to the dangerous properties of the anhydrous acid.

Fig. 44.



Properties.—Anhydrous hydrofluoric acid is a colorless, mobile liquid which fumes strongly in contact with the air. It may be cooled to —34° C. (—29.2° F.) without solidifying. Water absorbs the gaseous acid readily, forming a solution which, when saturated, possesses a sp. gr. of 1.25. This solution gives off a portion of its acid on distillation until the sp. gr. has decreased to 1.15, when it distils unchanged at 120° C. (248° F.), and contains from 36 to 38 per cent. of anhydrous acid. This acid of constant boiling-point does not correspond with any definite hydrate.

The concentrated acid when brought in contact with the skin produces dangerous wounds which are very difficult to heal. The vapor of the anhydrous acid when inhaled has been known to prove fatal.

Reactions.—1. Aqueous hydrofluoric acid dissolves many of the metals with evolution of hydrogen and formation of fluorides:

$$\underset{}{Fe} + \underset{\text{Hydrofluoric acid.}}{2HF} = \underset{\text{Ferrous fluoride.}}{\mathbf{FeF_2}} + H_2.$$

2. It acts upon silicic anhydride and silicates, forming silicic fluoride and water:

$$\underset{\text{Silicic anhydride.}}{\mathbf{SiO_2}} + \underset{\text{Hydrofluoric acid.}}{4HF} = \underset{\text{Silicic fluoride.}}{\mathbf{SiF_4}} + \underset{\text{Water.}}{\mathbf{2OH_2}}.$$

Thus hydrofluoric acid dissolves glass. This characteristic property is employed as a test for hydrofluoric acid and fluorides. All metallic fluorides, when treated with sulphuric acid, evolve hydrofluoric acid. The substance to be tested is placed in a small platinum or leaden dish with concentrated sulphuric acid, and the dish is covered with a piece of glass coated with wax, on which characters have been traced, so as to remove the wax from the parts written upon. The vessel is very gently warmed, and the glass is allowed to remain over it for about a quarter of an hour. On removing the wax, the presence of hydrofluoric acid will be indicated by the etching of the exposed parts of the glass. This method is frequently employed in etching scales on glass, the fumes from a mixture of powdered fluorspar and sulphuric

acid being employed for this purpose. Etchings produced by means of the aqueous solution of the acid are transparent and cannot be seen at a distance; when the gaseous acid is employed, the etched surface is dull, for which reason the use of the gaseous acid is preferred.

It is evident from the above that neither glass nor porcelain vessels can be employed in the preparation or storing of hydrofluoric acid. The aqueous solution is generally kept in vessels of caoutchouc or guttapercha.

Pure and perfectly dry hydrofluoric acid is without action upon glass (Gore); but the slightest trace of moisture induces the action just described.

Fluorides.—The fluorides are formed by dissolving metals in hydrofluoric acid or by acting with this acid on oxides, hydrates, or carbonates. The fluorides of the alkalies and of silver are soluble; those of the alkaline earths are insoluble. Nearly all the fluorides form molecular compounds with hydrofluoric acid, such as the double fluoride of hydrogen and potassium already mentioned.

CHAPTER XXIX.

TETRAD ELEMENTS.

Section I. (*Continued from* Chapter XXV.).

SILICON, *Silicium*, Si.

Atomic weight = 28.2. *Sp. gr.* (*crystallized*) = 2.49. *Atomicity* ^{iv}, *also a pseudo-triad. Evidence of atomicity:*

Silicic chloride, ...	$Si^{iv}Cl_4$.
Silicic fluoride, ...	$Si^{iv}F_4$.
Disilicic hexachloride, . . .	$\left\{\begin{matrix} SiCl_3 \\ SiCl_3. \end{matrix}\right.$

History.—Silicon was first isolated by Berzelius in 1810.

Occurrence.—Silicon is, with the exception of oxygen, the most abundant and widely distributed of the elements. It does not occur in the free state. In combination with oxygen it forms the mineral quartz or silica, which is the anhydride of silicic acid: whilst the compounds of silica with bases constitute the chief constituents of the rocks which compose the earth's crust, and consequently of the soils, which have all been produced by the disintegration of the rocks. From the soils the silicon is absorbed by plants, in the ashes of which it may always be detected.

Preparation.—1. Silicon is liberated when silicic anhydride is reduced by heating it with sodium:

$$\underset{\text{Silicic anhydride.}}{SiO_2} + 2Na_2 = Si + \underset{\text{Sodic oxide.}}{2ONa_2}.$$

This method is not, however, adapted for the preparation of pure silicon. The reaction may be shown by heating sodium in a test-tube of Bohemian glass, when the glass speedily blackens owing to the reduction of the silica.

2. Pure silicon may be readily obtained by heating potassic silicofluoride with potassium:

$$\underset{\text{Potassic silicofluoride.}}{SiK_2F_6} + 2K_2 = Si + \underset{\text{Potassic fluoride.}}{6KF}.$$

Sodium may be substituted for potassium in this reaction. The fused mass is allowed to cool, and the potassic fluoride is then dissolved in water, when the silicon remains behind as a brown amorphous powder.

3. Silicon is deposited in the same amorphous condition when sodium is heated in a current of the vapor of silicic chloride:—

$$\underset{\text{Silicic chloride.}}{SiCl_4} + 2Na_2 = Si + \underset{\text{Sodic chloride.}}{4NaCl}.$$

4. In order to obtain silicon in the crystallized condition, advantage is taken of the property which this element possesses of dissolving at a high temperature in certain metals, such as zinc or aluminium, and crystallizing from these metallic solutions on cooling. A mixture of 15 parts of dry potassic silicofluoride, with 4 parts of sodium in thin slices, is thrown into a red-hot Hessian crucible; 36 parts of granulated zinc are quickly added, and the mass is covered with a layer of fused sodic chloride. The lid is then replaced and the whole is heated for some time to a temperature below the boiling point of zinc. On dissolving the cooled regulus of zinc in acids, the crystallized silicon remains behind.

5. Crystallized silicon may also be obtained by heating together in a crucible 1 part of aluminium with 5 parts of glass free from lead, and 10 parts of powdered cryolite ($('\mathbf{Al}'''_2F_6,6NaF)$). The silica of the glass is reduced at the expense of the aluminium.

Properties.—Amorphous silicon is a brown powder, devoid of lustre. It inflames when heated in the air, but cannot be entirely burnt, even in oxygen, as the silica which is formed coats the particles and prevents further oxidation. It is insoluble in water, and is not attacked by acids, except hydrofluoric acid, which dissolves it readily. When heated with exclusion of air it becomes denser, and is no longer combustible.

Crystallized silicon forms dark lustrous octahedra, which possess a sp. gr. of 2.49 and are hard enough to scratch glass. It may be heated to whiteness in oxygen without burning. At a very high temperature it fuses. It conducts electricity imperfectly. Acids are without action upon it, with the exception of a mixture of nitric and hydrofluoric acids, which dissolves it slowly.

Reactions.—1. When amorphous silicon is heated in oxygen, silicic anhydride is formed.

2. Both varieties of silicon may be burned in a stream of chlorine, silicic chloride being produced. Owing to the volatile nature of the silicic chloride, the whole of the silicon may be thus converted.

3. When amorphous silicon is treated with hydrofluoric acid, or the crystallized variety with a mixture of nitric and hydrofluoric acids, hydrofluosilicic acid is formed:—

$$Si + \underset{\substack{\text{Hydrofluoric}\\ \text{acid.}}}{6HF} = \underset{\substack{\text{Hydrofluo-}\\ \text{silicic acid.}}}{SiH_2F_6} + 2H_2.$$

4. Amorphous silicon when boiled with caustic alkalies, yields an alkaline silicate, with evolution of hydrogen:—

$$Si + \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{4KHo} = \underset{\substack{\text{Potassic}\\ \text{silicate.}}}{\mathbf{SiKo_4}} + 2H_2.$$

Crystallized silicon must be fused with the alkali in order that this reaction may take place.

COMPOUND OF SILICON WITH HYDROGEN.

SILICIC HYDRIDE, *Siliciuretted Hydrogen.*

$$\mathbf{SiH_4}.$$

Molecular weight = 32.2. *Molecular volume* $\square\square$.

Preparation.—1. When dilute sulphuric acid is decomposed by a feeble electric current passing from electrodes of aluminium containing silicon, silicic anhydride is evolved at the negative electrode.

2. It may also be obtained by decomposing magnesic silicide with hydrochloric acid:

$$\underset{\substack{\text{Magnesic}\\ \text{silicide.}}}{\mathbf{SiMg''_2}} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl} = \underset{\substack{\text{Magnesic}\\ \text{chloride.}}}{\mathbf{2MgCl_2}} + \underset{\substack{\text{Silicic}\\ \text{hydride.}}}{\mathbf{SiH_4}}.$$

The magnesic silicide is prepared by heating together in a closed crucible 40 parts of anhydrous magnesic chloride, 35 parts of dried sodic silicofluoride, 10 parts of fused sodic chloride, and 20 parts of sodium in thin slices. The fused mass is broken into fragments and introduced into a flask fitted with safety and delivery tubes. The flask and the delivery tube are filled with water from which the air has been expelled by boiling, and hydrochloric acid is then poured through the funnel of the safety tube into the flask. Silicic hydride is evolved and is collected over previously boiled water in the pneumatic trough.

3. Silicic hydride prepared by either of the foregoing processes is always contaminated with hydrogen; but if ethylic silico-orthoformate, a substance obtained by the action of silicon-chloroform (*q.v.*) on absolute alcohol, be placed in contact with sodium, it breaks up into ethylic orthosilicate and pure silicic hydride, the sodium remaining unaffected:

$$\underset{\text{Ethylic silico-orthoformate.}}{4\mathbf{Si}H(C_2H_5O)_3} = \underset{\text{Silicic hydride.}}{\mathbf{Si}H_4} + \underset{\text{Ethylic orthosilicate.}}{3\mathbf{Si}(C_2H_5O)_4}.$$

Properties.—Silicic hydride is a colorless gas. When prepared from magnesic silicide it inflames spontaneously in contact with air, and burns with a brilliant white flame evolving dense clouds of silicic anhydride. The pure gas is not spontaneously inflammable, but it acquires this property when it is gently warmed, or when the pressure is reduced, or when it is diluted with hydrogen.

Reactions.—1. Burned in the air or oxygen, silicic hydride yields silicic anhydride and water:

$$\underset{\text{Silicic hydride.}}{\mathbf{Si}H_4} + 2O_2 = \underset{\text{Silicic anhydride.}}{\mathbf{Si}O_2} + \underset{\text{Water.}}{2OH_2}.$$

2. With chlorine it explodes spontaneously, forming silicic chloride and hydrochloric acid:

$$\underset{\text{Silicic hydride.}}{\mathbf{Si}H_4} + 4Cl_2 = \underset{\text{Silicic chloride.}}{\mathbf{Si}Cl_4} + \underset{\text{Hydrochloric acid.}}{4HCl}.$$

3. When heated, it is decomposed into amorphous silicon and free hydrogen, the latter occupying twice the volume of the original gas.

4. It is decomposed at ordinary temperatures by a solution of potassic hydrate, yielding four times its volume of hydrogen:

$$\underset{\text{Silicic hydride.}}{\mathbf{Si}H_4} + \underset{\text{Potassic hydrate.}}{2KHo} + \underset{\text{Water}}{OH_2} = \underset{\text{Potassic silicate.}}{\mathbf{Si}OKo_2} + 4H_2.$$

5. It precipitates some of the heavy metals in the form of silicides from the solutions of their salts:

$$\underset{\text{Cupric sulphate.}}{2\mathbf{S}O_2Cuo''} + \underset{\text{Silicic hydride.}}{\mathbf{Si}H_4} = \underset{\text{Cupric silicide.}}{\mathbf{Si}Cu''_2} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2}.$$

COMPOUNDS OF SILICON WITH THE HALOGENS.

SILICIC CHLORIDE.

$SiCl_4$.

Molecular weight = 170.2. *Molecular volume* $\square\square$. 1 *litre of the vapor weighs* 85.1 *criths. Sp. gr. of liquid* 1.52. *Boils at* 59° C. (138.2° F.).

Preparation.—1. Silicic chloride is formed by the direct combination of its elements when silicon is burnt in chlorine.

2. It is most conveniently prepared by heating a mixture of finely divided carbon and silicic anhydride in a stream of dry chlorine:

$$\underset{\substack{\text{Silicic}\\ \text{anhydride.}}}{SiO_2} + 2C + 2Cl_2 = \underset{\substack{\text{Silicic}\\ \text{chloride.}}}{SiCl_4} + \underset{\substack{\text{Carbonic}\\ \text{oxide.}}}{2CO}.$$

Properties.—Silicon tetrachloride is a colorless mobile liquid, fuming strongly in contact with air.

Reaction.—Water decomposes it instantaneously with formation of silicic and hydrochloric acids:

$$\underset{\substack{\text{Silicic}\\ \text{chloride.}}}{SiCl_4} + \underset{\text{Water.}}{4OH_2} = \underset{\substack{\text{Silicic}\\ \text{acid.}}}{SiHo_4} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl}.$$

DISILICIC HEXACHLORIDE.

$$\begin{cases} SiCl_3 \\ SiCl_3 \end{cases}.$$

Molecular weight = 269.4. *Molecular volume* $\square\square$. 1 *litre of the vapor weighs* 134.7 *criths. Sp. gr. of liquid* 1.58. *Fuses at* —1° C. (30.2° F.). *Boils at* 147° C. (296.6° F.).

Preparation.—1. This compound is formed in small quantity when the vapor of silicic chloride is passed over silicon heated above 1000° C.:

$$\underset{\substack{\text{Silicic}\\ \text{chloride.}}}{3SiCl_4} + Si = \underset{\substack{\text{Disilicic}\\ \text{hexachloride.}}}{2\begin{cases} SiCl_3 \\ SiCl_3 \end{cases}}.$$

2. It is more easily prepared by gently heating disilicic hexiodide (*q.v.*) with mercuric chloride:

$$\underset{\substack{\text{Disilicic}\\ \text{hexiodide.}}}{\begin{cases} SiI_3 \\ SiI_3 \end{cases}} + \underset{\substack{\text{Mercuric}\\ \text{chloride.}}}{3HgCl_2} = \underset{\substack{\text{Disilicic}\\ \text{hexachloride}}}{\begin{cases} SiCl_3 \\ SiCl_3 \end{cases}} + \underset{\substack{\text{Mercuric}\\ \text{iodide.}}}{3HgI_2}.$$

Properties.—Disilicic hexachloride is a mobile, colorless liquid, which at a temperature of —1° C. solidifies to a crystalline mass. It possesses the peculiarity of being stable only below 350° C. and above 1000° C., whilst at intermediate temperatures it dissociates into silicic chloride and silicon. A similar abnormal behavior has already been noted in the case of seleniuretted and telluretted hydrogen.

Reaction.—With water it is decomposed into *silicon-oxalic acid* and hydrochloric acid:

$$\underset{\substack{\text{Disilicic}\\ \text{hexachloride.}}}{\left\{\begin{array}{l}SiCl_3\\ SiCl_3\end{array}\right.} + \underset{\text{Water.}}{4OH_2} = \underset{\substack{\text{Silicon-oxalic}\\ \text{acid.}}}{\left\{\begin{array}{l}SiOHo\\ SiOHo\end{array}\right.} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{6HCl.}$$

SILICON CHLOROFORM, *Silicic Hydrotrichloride.*

$SiHCl_3$.

Molecular weight = 135.7. *Molecular volume* $\square\!\square$. 1 *litre of the vapor weighs* 67.85 *criths*. *Sp. gr. of liquid* 1.6. *Boils at* 36° C. (96.8° F.)

Preparation.—Silicon chloroform is formed when silicon is heated to dull redness in a current of hydrochloric acid gas:

$$Si + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{3HCl} = \underset{\substack{\text{Silicon}\\ \text{chloroform.}}}{SiHCl_3} + H_2.$$

Properties.—Silicon chloroform is a colorless liquid. It is very inflammable, and burns with a green-edged flame. A mixture of its vapor with air explodes in contact with a heated body.

Reactions.—1. It is decomposed by chlorine at ordinary temperatures:

$$\underset{\substack{\text{Silicon}\\ \text{chloroform.}}}{SiHCl_3} + Cl_2 = \underset{\substack{\text{Silicic}\\ \text{chloride.}}}{SiCl_4} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl.}$$

2. By contact with water it is transformed into *silicoformic anhydride*, or *disilicic hydrotrioxide*:

$$\underset{\substack{\text{Silicon}\\ \text{chloroform.}}}{2SiHCl_3} + \underset{\text{Water.}}{3OH_2} = \underset{\substack{\text{Silicoformic}\\ \text{anhydride.}}}{\left\{\begin{array}{l}SiHO\\ O\\ SiHO\end{array}\right.} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{6HCl.}$$

Silicon bromoform, $SiHBr_3$, and *silicon iodoform*, $SiHI_3$, have also been prepared.

SILICIC BROMIDE.

$SiBr_4$.

Molecular weight = 348.2. *Molecular volume* $\square\!\square$. *Fuses at* —13° C. (6.6° F.). *Boils at* 153° C. (307.4° F.). *Sp. gr. of liquid* 2.813 *at* 0° C.

Preparation.—This substance is obtained by a method analogous to that employed in the preparation of the chloride, bromine-vapor being substituted for chlorine.

Properties.—It is a fuming, colorless liquid.

Reaction.—Water decomposes it with formation of silicic and hydrobromic acids:

$$\underset{\substack{\text{Silicic}\\ \text{bromide.}}}{SiBr_4} + \underset{\text{Water.}}{4OH_2} = \underset{\substack{\text{Silicic}\\ \text{acid.}}}{SiHo_4} + \underset{\substack{\text{Hydrobromic}\\ \text{acid.}}}{4HBr.}$$

Disilicic hexabromide, $\left\{\begin{array}{l}SiBr_3\\ SiBr_3\end{array}\right.$, is also known.

SILICIC IODIDE.

SiI_4.

Molecular weight = 536.2. *Molecular volume* $\square\!\square$. *Fuses at* 120.5° C. (248.9° F.). *Boils in carbonic anhydride at* 290° C. (554° F.).

Preparation.—This compound is formed by the direct union of its elements when a mixture of iodine vapor and carbonic anhydride is passed over red-hot silicon. The

carbonic anhydride serves to carry off the vapor of the silicic iodide as fast as it is formed, and thus to prevent its decomposition.

Properties.—Silicic iodide crystallizes in colorless octahedra. It may be distilled in a current of carbonic anhydride. It is soluble in carbonic disulphide.

Reactions.—1. Water decomposes it into silicic and hydriodic acids.

2. Absolute alcohol decomposes it, with production of silicic anhydride, ethylic iodide, and hydriodic acid:

$$\underset{\substack{\text{Silicic}\\\text{iodide.}}}{\mathbf{SiI_4}} + \underset{\text{Alcohol.}}{2EtHo} = \underset{\substack{\text{Silicic}\\\text{anhydride.}}}{\mathbf{SiO_2}} + \underset{\substack{\text{Ethylic}\\\text{iodide.}}}{2EtI} + \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{2HI.}$$

Disilicic hexiodide, $\left\{\begin{matrix}\mathbf{SiI_3}\\\mathbf{SiI_3}\end{matrix}\right.$, has been obtained by heating silicic iodide with finely divided silver:

$$\underset{\substack{\text{Silicic}\\\text{iodide.}}}{2\mathbf{SiI_4}} + Ag_2 = \underset{\substack{\text{Disilicic}\\\text{hexiodide.}}}{\left\{\begin{matrix}\mathbf{SiI_3}\\\mathbf{SiI_3}\end{matrix}\right.} + \underset{\substack{\text{Argentic}\\\text{iodide.}}}{2AgI.}$$

It forms hexagonal crystals, fusing with decomposition at 250° C.

SILICIC FLUORIDE.

$\mathbf{SiF_4}$.

Molecular weight = 104.2. *Molecular volume* $\square\square$. 1 *litre weighs* 52.1 *criths. Fuses at* —140° C. (—220° F.). *Boils at* —107° C. (—160.6° F.).

Preparation.—Silicic fluoride is prepared by heating together, in a flask furnished with a delivery tube, quartz sand, fluorspar, and an excess of concentrated sulphuric acid:

$$\underset{\substack{\text{Silicic}\\\text{anhydride.}}}{\mathbf{SiO_2}} + \underset{\substack{\text{Calcic}\\\text{fluoride.}}}{2\mathbf{CaF_2}} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2\mathbf{SO_2}Ho_2} = \underset{\substack{\text{Silicic}\\\text{fluoride.}}}{\mathbf{SiF_4}} + \underset{\substack{\text{Dihydric calcic}\\\text{sulphate.}}}{2SOHo_2Cao''.}$$

The gas may be collected in perfectly dry glass vessels over mercury.

Properties.—Silicic fluoride is a colorless gas with a very pungent odor. It fumes strongly in contact with air. Under a pressure of 30 atmospheres, or at a temperature of —107° C. (—160.6° F.), it condenses to a colorless liquid, which at a still lower temperature solidifies. It is not altered by exposure to the heat of powerful electric sparks.

Reaction.—Water decomposes it with formation of silicic and hydrofluosilicic acids:

$$\underset{\substack{\text{Silicic}\\\text{fluoride.}}}{3\mathbf{SiF_4}} + \underset{\text{Water.}}{4OH_2} = \underset{\substack{\text{Silicic}\\\text{acid.}}}{\mathbf{Si}Ho_4} + \underset{\substack{\text{Hydrofluosilicic}\\\text{acid.}}}{2SiH_2F_6.}$$

When the gas is passed into water, the silicic acid separates out as a gelatinous mass, whilst the hydrofluosilicic acid remains in solution. To prevent the delivery tube from being stopped up, it must dip under mercury at the bottom of the vessel in which the water is contained. The liquid is afterwards filtered from the silicic acid and evaporated at

a low temperature. The aqueous solution of hydrofluosilicic acid thus obtained forms a fuming acid liquid, which on further evaporation decomposes into silicic fluoride and hydrofluoric acid.

With metallic oxides, hydrates, and some salts, hydrofluosilicic acid produces silicofluorides:

$$\underset{\text{Hydrofluosilicic acid.}}{SiH_2F_6} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic silicofluoride.}}{SiK_2F_6} + \underset{\text{Water.}}{2OH_2}.$$

In contact with an excess of base the silicofluorides are decomposed, yielding silicates and fluorides:

$$\underset{\text{Potassic silicofluoride.}}{SiK_2F_6} + \underset{\text{Potassic hydrate.}}{8KHo} = \underset{\text{Potassic silicate.}}{SiKo_4} + \underset{\text{Potassic fluoride.}}{6KF} + \underset{\text{Water.}}{4OH_2}.$$

The silicofluorides of barium and potassium are insoluble in water.

Disilicic hexafluoride has been prepared by passing silicic fluoride over melted silicon;

$$\underset{\text{Silicic fluoride.}}{3SiF_4} + Si = \underset{\text{Disilicic hexafluoride.}}{2\left\{\begin{matrix} SiF_3 \\ SiF_3 \end{matrix}\right.}.$$

It forms a fine white powder.

COMPOUNDS OF SILICON WITH OXYGEN AND HYDRYOXYL.

Silicic anhydride, ...	SiO_2.
Silicic acid, ...	$SiHo_4$ and $SiOHo_2$.

Other Modifications of Silicic Acid.

$Si_2O_3Ho_2$	$Si_6O_{10}Ho_4$
$Si_3O_5Ho_2$	$Si_6O_8Ho_8$
$Si_4O_7Ho_2$	$Si_8O_{15}Ho_2$
$Si_4O_4Ho_8$.	

SILICIC ANHYDRIDE, *Silica.*

SiO_2.

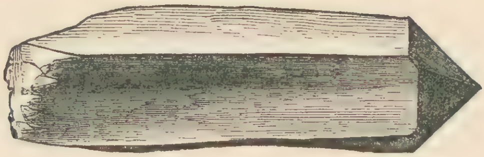
Molecular weight = 60.2. *Sp. gr.* (*amorphous*) 2.2; (*tridymite*), 2.3, (*quartz*) 2.69.

Occurrence.—Some of the forms in which silicic anhydride is found in nature have already been alluded to (p. 309). It occurs in the crystallized condition as quartz and tridymite, and in an amorphous form as opal.

Preparation.—It may be obtained by heating silicic acid to 100° C. Water is given off and amorphous silicic anhydride remains.

Properties.—As quartz or rock crystal, silicic anhydride occurs in the form of hexagonal prisms terminated by a hexagonal pyramid (Fig. 45). The crystals are sometimes colorless, sometimes colored by the presence of various oxides. Amethyst quartz, rose quartz, smoky quartz, are

FIG. 45.



varieties of this description named according to their color. Occasionally quartz occurs in large crystalline masses as quartzose rock. It has a sp. gr. of 2.69, and is hard enough to scratch glass.

Tridymite is a second crystallized variety of silicic anhydride found in various trachytic rocks. Like rock crystal, it crystallizes in forms belonging to the hexagonal system; but the relations of the axes vary in the two minerals, so that the forms of the one cannot be referred to those of the other. The sp. gr. of tridymite is 2.3.

Amorphous silicic anhydride, when artificially prepared, forms a white, very fine powder. As opal, amorphous silica occurs in transparent or translucent masses with a conchoidal fracture. The sp. gr. of the artificial variety is 2.2; that of the natural 2.3.

Silicic anhydride in all its forms is insoluble in water at ordinary temperatures. It dissolves slightly, however, if heated with water under pressure to low redness, and, on cooling, crystallizes from the solution in the form of quartz. In like manner, when a solution of an alkaline silicate is heated in a sealed glass tube, a portion of the silica from the glass is dissolved, forming an acid silicate. On cooling, the excess of silica separates out. If the separation takes place above 180° C. (356° F.) the silica is obtained as quartz; below this temperature tridymite is formed; at ordinary temperatures it is deposited in the hydrated condition as amorphous silicic acid.

Acids, with the exception of hydrofluoric, are without action upon silicic anhydride. With aqueous hydrofluoric acid hydrofluo-silicic acid is formed:

$$\underset{\text{Silicic anhydride.}}{\mathbf{Si}O_2} + \underset{\text{Hydrofluoric acid.}}{6HF} = \underset{\text{Hydrofluosilicic acid.}}{SiH_2F_6} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

All the modifications of silicic anhydride, when fused with an excess of a caustic alkali or an alkaline carbonate, combine with the base to form a soluble silicate:

$$\underset{\text{Silicic anhydride.}}{\mathbf{Si}O_2} + \underset{\text{Sodic carbonate.}}{2\mathbf{CO}Nao_2} = \underset{\text{Sodic silicate.}}{\mathbf{Si}Nao_4} + \underset{\text{Carbonic anhydride.}}{2\mathbf{C}O_2}.$$

The amorphous variety, if it has not been ignited too strongly, dissolves in boiling solutions of caustic alkalies.

SILICIC ACID.

Tetrabasic, . . $\mathbf{Si}Ho_4$, Dibasic, . . . $\mathbf{Si}OHo_2$.

Preparation.—1. Silicic acid may be obtained by decomposing a solution of sodic or potassic silicate with hydrochloric acid:

$\mathbf{Si}Nao_4$	+	$4HCl$	=	$\mathbf{Si}Ho_4$	+	$4NaCl$.
Sodic silicate.		Hydrochloric acid.		Silicic acid.		Sodic chloride.

If the solution of the alkaline silicate is concentrated, the silicic acid separates out as a white gelatinous precipitate; but if a dilute solution of the silicate be poured into an excess of hydrochloric acid, the silicic acid remains dissolved. The clear solution obtained by the latter method may be freed from the sodic chloride and excess of hydrochloric acid by dialysis (see Introductions p. 130). The silicic acid, being a colloid, is unable to pass through the membrane of the dialyzer, whilst the other substances in solution diffuse freely through into the surrounding liquid. The solution of silicic acid may be concentrated by boiling in a flask until it contains 22 per cent. of the tetrabasic acid, but beyond this point it solidifies to a jelly. When evaporated in a dish the solution is apt to gelatinize round the edges, and then the whole mass solidifies. The concentrated solution also gelatinizes spontaneously when allowed to stand for a few days, and the same effect is produced instantaneously by passing carbonic anhydride into the solution, or by the addition of a trace of an alkaline carbonate.

2. Gelatinous silicic acid may be obtained by passing a stream of carbonic anhydride through a solution of an alkaline silicate:

$\mathbf{Si}Nao_4$	+	$4OH_2$	+	$4\mathbf{C}O_2$	=	$\mathbf{Si}Ho_4$	+	$4\mathbf{C}OHoNao$.
Sodic silicate.		Water.		Carbonic anhydride.		Silicic acid.		Hydric sodic carbonate.

A reaction similar to this is the cause of the disintegration of granitic rocks. The carbonic anhydride which is held in solution in all natural waters acts upon the alkaline silicates contained in the rocks.

3. Gelatinous silicic acid is also formed when silicic fluoride is passed into water (p. 315).

Properties.—Silicic acid, like most other weak polybasic acids of even basicity, has a great tendency to give off water and form an anhydride. It is therefore exceedingly doubtful whether any of the silicic acids have been prepared in a state of purity. By allowing gelatinous silicic acid to dry in the air, a compound having approximately the composition represented by the formula $\mathbf{Si}_6O_8Ho_8$ is obtained, and this, when dried at 100° C., parts with more water, yielding a hydrate of the formula $\mathbf{Si}_6H_{10}Ho_4$. These substances are, however, very difficult to obtain of

fixed composition, and they possess none of the other characteristics of definite chemical compounds.

Silicates.—The preparation of alkaline silicates has already been described (p. 317).

Silica and the silicates form a very important class of minerals. The following list contains a few examples:

Sand, Flint, Rock crystal, Quartz, Opal, Chalcedony } *Silicic anhydride*, ...	SiO_2.
Peridote (*Dimagnesic silicate*), ...	$SiMgo''_2$.
Phenacite (*Diberyllic silicate*), ...	$SiBeo''_2$.
Willemite (*Dizincic silicate*), ...	$SiZno''_2$.
Zircon (*Zirconic silicate*), ...	$SiZro^{iv}$.
Enstatite (*Monomagnesic silicate*), ...	$SiOMgo''$.
Yorke's Sodic silicate, ...	$\left\{\begin{array}{l}SiNao_3\\O\\SiNao_3\end{array}\right.$.
Ophite (Noble Serpentine), ...	$\left\{\begin{array}{l}Si\\O\\Si\end{array}\right. Mgo''_3$.
Diopside (*Calcic magnesic disilicate*), . . .	$\left\{\begin{array}{l}Si\\Si\end{array}\right. Cao''Mgo''$.
Talc (*Tetramagnesic pentasilicate*), . . .	$Si_5O_6Mgo''_4$.
Okenite (*Tetrahydric calcic disilicate*), . .	$\left\{\begin{array}{l}SiHo_2\\O\\SiHo_2\end{array}\right. Cao''$.
Serpentine (*Dihydric trimagnesic disilicate*),	$\left\{\begin{array}{l}SiHoMgo''\\Mgo''\\SiHoMgo''\end{array}\right.$.
Steatite (*Trimagnesic tetrasilicate*), . . .	$Si_4O_5Mgo''_3$.
Meerschaum (*Tetrahydric dimagnesic trisilicate*), ...	$\left\{\begin{array}{l}SiHoMgo''\\O\\SiHo_2\\O\\SiHoMgo''\end{array}\right.$.
Pyrophyllite (*Dihydric aluminic tetrasilicate*), ...	$\left\{\begin{array}{l}SiOHo\\SiO\\SiO\\SiOHo\end{array}\right. Alo^{vi}$.*
Anorthite (*Aluminic calcic disilicate*), . . .	$Si_2('Al'''_2O_6)^{vi}Cao''$.
Labradorite (*Aluminic calcic trisilicate*), . .	$\left\{\begin{array}{l}SiO\\SiCao''—Alo^{vi}\\SiO\end{array}\right.$.

* $Alo^{vi} = ('Al'''_2O_6)^{vi}$.

Grossularia (*Aluminic tricalcic trisilicate*), . $\left\{\begin{array}{l} SiCao''— \\ SiCao''—Alo^{vi}. \\ SiCao''— \end{array}\right.$

Emerald (*Triberyllic aluminic hexasilicate*), . $Si_6O_6Alo^{vi}Beo''_3$.

Chloropal (*Ferric trisilicate*), ... $\left\{\begin{array}{l} SiO— \\ SiO—Feo^{vi},3OH_2.* \\ SiO— \end{array}\right.$

Felspar. Orthose (*Dipotassic aluminic hexasilicate*), ... $Si_6O_8Ko_2Alo^{vi}$.

COMPOUNDS OF SILICON CONTAINING SULPHUR.

SILICIC SULPHIDE.

SiS''_2.

Preparation.—1. Silicic sulphide is formed by the direct union of its elements when amorphous silicon is heated in sulphur vapor.

2. It is more conveniently obtained by passing the vapor of carbonic disulphide over a mixture of silicic anhydride and charcoal heated to redness:

$$\underset{\text{Silicic anhydride.}}{SiO_2} + \underset{\text{Carbonic disulphide.}}{CS_2} + C = \underset{\text{Silicic sulphide.}}{SiS''_2} + \underset{\text{Carbonic oxide.}}{2CO}.$$

Properties.—Silicic sulphide forms white silky needles resembling asbestos in appearance. It may be sublimed without decomposition. In contact with water it forms silicic acid and sulphuretted hydrogen:

$$\underset{\text{Silicic sulphide.}}{SiS''_2} + \underset{\text{Water.}}{4OH_2} = \underset{\text{Silicic acid.}}{SiHo_4} + \underset{\text{Sulphuretted hydrogen.}}{2SH_2}.$$

SILICIC TRICHLORSULPHHYDRATE.

$SiCl_3Hs$.

Molecular weight = 167.7. *Molecular volume* $\boxed{}\boxed{}$. *Boils at* 96° C. (204.8° F.).

Preparation.—This compound is obtained by passing a mixture of silicic chloride vapor and sulphuretted hydrogen through a red-hot porcelain tube:

$$\underset{\text{Silicic chloride.}}{SiCl_4} + \underset{\text{Sulphuretted hydrogen.}}{SH_2} = \underset{\text{Silicic trichlorsulphhydrate.}}{SiCl_3Hs} + \underset{\text{Hydrochloric acid.}}{HCl}.$$

Properties.—Silicic trichlorsulphhydrate is a colorless fuming liquid, boiling at 96° C. (204.8° F.). Water decomposes it, forming silicic acid, hydrochloric acid, and sulphuretted hydrogen:

$$\underset{\text{Silicic trichlorsulphhydrate.}}{SiCl_3Hs} + \underset{\text{Water.}}{4OH_2} = \underset{\text{Silicic acid.}}{SiHo_4} + \underset{\text{Hydrochloric acid.}}{3HCl} + \underset{\text{Sulphuretted hydrogen.}}{SH_2}.$$

* $Feo^{vi} = ('Fe'''_2O_6)^{vi}$.

TIN, Sn.*

Atomic weight = 118. *Sp. gr.* 7.28. *Fuses at* 228° C. (442.4° F.). *Atomicity* $''$ and ^{iv}, *and also a pseudo-triad. Evidence of atomicity:*

Stannous chloride (at 900° C.), ... $Sn''Cl_2$.
Stannic chloride, ... $Sn^{iv}Cl_4$.

History.—Tin has been known from the earliest historical times. The tin-mines of Cornwall were celebrated before the Roman invasion, and from these the Phœnician merchants supplied the metal to the ancient world.

Occurrence.—Tin is never found in the free or native state. In combination with oxygen as tin-stone or stannic anhydride, it occurs in veins in the primitive rocks, and sometimes in alluvial deposits (stream tin). Tin-stone is the only ore from which the metal is extracted. The mines of Cornwall, above referred to, and those of Devonshire, furnish the chief supply; those of Malacca and Banca come next in importance.

Extraction.—The tin-stone is first crushed and washed in order to free it from earthy impurities. It is then roasted in a reverberatory furnace, by which means the iron- and copper-pyrites with which it is contaminated are oxidized. The iron is thus converted into ferric oxide, with evolution of sulphurous anhydride, whilst the copper forms cupric sulphate. The roasted mass is again washed, the cupric sulphate being thus dissolved and the ferric oxide mechanically removed. The finely divided tin-stone thus purified is mixed with charcoal and reduced in a furnace:

$$\underset{\text{Stannic anhydride.}}{SnO_2} + C_2 = Sn + \underset{\text{Carbonic oxide.}}{2CO}.$$

The tin obtained by the above process is generally contaminated with various foreign metals (iron, copper, lead, arsenic, antimony), from which it may be separated by liquation. This process consists in melting the crude tin at the lowest possible temperature on the bed of a reverberatory furnace. The tin, by virtue of its lower fusing-point, melts first, and flows off, leaving a less fusible alloy of tin with the other metals.

Properties.—Tin is a white metal with a high metallic lustre. When warm it emits a peculiar odor. In hardness it is intermediate between lead and zinc. It is malleable and may be beaten into thin leaves (tin-foil). At a temperature of 200° C. it becomes brittle. It fuses at 228° C. (442.4° F.), and when exposed to the air in a molten condition

* This element, whilst exhibiting all the physical properties of a metal, behaves in most of its chemical relations like a non-metal. Its compounds resemble those of carbon, silicon, and titanium, and it can be most conveniently studied in connection with these elements. For similar reasons antimony, bismuth, and a few other metallic elements have, in the present work, been classed with the non-metals.

undergoes superficial oxidation. At a white heat it enters into ebullition and burns with a brilliant white light, forming stannic anhydride. It is also oxidized when heated to redness in a current of steam. At ordinary temperature it resists the action of air and moisture.

If a bar of tin be bent backwards and forwards a faint crackling sound is heard, and the point of flexure becomes hot. These effects depend upon the breaking and friction of the crystals within the mass. The crystalline structure of tin may be readily shown by brushing the surface of a piece of the metal (which has been cast but not hammered) with warm dilute aqua-regia, when it becomes covered with fine crystalline markings, resembling in appearance, watered silk. Tin thus prepared was formerly much used for ornamental purposes under the name of *moirée métallique*. Crystals of tin may be readily obtained by fusing a large quantity of the metal, allowing it partially to solidify in the crucible, then breaking a hole in the crust which forms on the surface, and pouring out the molten metal. The interior of the crucible will be found to be lined with crystals of tin.

Reactions.—1. Hot concentrated hydrochloric acid dissolves tin with evolution of hydrogen and formation of stannous chloride :

$$\underset{}{Sn} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Stannous chloride.}}{\mathbf{Sn}Cl_2} + H_2.$$

2. Heated with concentrated sulphuric acid it forms stannous sulphate, sulphurous anhydride being evolved :

$$Sn + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2} = \underset{\text{Stannous sulphate.}}{\mathbf{S}O_2\mathbf{Sn}o''} + \underset{\text{Sulphurous anhydride.}}{\mathbf{S}O_2} + \underset{\text{Water.}}{2OH_2}.$$

3. Nitric acid of sp. gr. 1.3 acts upon it violently, oxidizing it to metastannic acid ($\mathbf{Sn}_5O_5Ho_{10}$). Nitric acid of sp. gr. 1.5 does not attack tin.

4. Cold dilute nitric acid dissolves it slowly without evolution of gas, stannous nitrate being formed. At the same time a portion of the nitric acid undergoes reduction to ammonia, which combines with the excess of nitric acid :

$$4Sn + \underset{\text{Nitric acid.}}{9\mathbf{N}O_2Ho} = \underset{\text{Stannous nitrate.}}{4\begin{matrix}\mathbf{N}O_2\\ \mathbf{N}O_2\end{matrix}\mathbf{Sn}o''} + \underset{\text{Ammonia.}}{\mathbf{N}H_3} + \underset{\text{Water.}}{3OH_2}.$$

5. Caustic alkalies dissolve tin when fused with it, a soluble stannate being formed, whilst hydrogen is evolved :

$$Sn + \underset{\text{Potassic hydrate.}}{2OKH} + \underset{\text{Water.}}{OH_2} = \underset{\text{Potassic stannate.}}{\mathbf{Sn}OKo_2} + 2H_2.$$

6. It combines directly with sulphur, phosphorus, chlorine, bromine, and iodine.

USES.—*Tinning.*—Tin is frequently employed in coating other metals to preserve them from rust, a process known as *tinning*. Ordinary tin-plate is iron which has been thus treated. The surface of the metal to be tinned is thoroughly freed from every trace of oxide, which would otherwise prevent the adhesion of the tin, and the metal is then plunged into a bath of melted tin, covered with a layer of grease to exclude the air. The film of tin which adheres to the surface forms an alloy with the metal, and cannot be separated from it mechanically. The tinning of copper is effected in a similar manner.

Alloys.—Numerous alloys of tin are employed in the arts. *Plumber's solder* is an alloy of tin and lead, the proportion of tin increasing with the degree of fusibility required.* *Fine solder* consists of 2 parts of tin and 1 of lead; *common solder* of equal parts of tin and lead; and *coarse solder* of 1 of tin and 2 of lead. *Britannia metal* consists of equal parts of brass, tin, and antimony, and is employed as a cheap substitute for silver in the manufacture of teapots, etc. *Pewter* is a similar alloy, in which, however, the lead and tin greatly predominate. The alloys of tin with copper will be treated of under the heading of the latter metal.

COMPOUNDS OF TIN.

The following are the names and probable constitutional formulæ of the principal compounds of this metal:

Stannous chloride (at 900°),	$SnCl_2$.	
Stannic chloride, . . .	$SnCl_4$.	
Stannous oxide, ...	SnO.	
Stannic oxide or anhydride,	SnO_2.	
Stannous oxydichloride″, .	$\left\{\begin{matrix} SnO \\ SnCl_2 \end{matrix}\right.$.	$O=Sn=Sn<^{Cl}_{Cl}$.
Stannous hydrate, . . .	$SnHo_2$.	$Sn<^{O-H}_{O-H}$.
Stannic acid, ...	$SnOHo_2$.	$H-O-\overset{\overset{O}{\Vert}}{Sn}-O-H$.
Potassic stannite, . . .	$SnKo_2$.	
Dipotassic stannate, . . .	$SnOKo_2,4OH_2$.	
Distannic trioxide, . . .	$\left\{\begin{matrix} SnO \\ SnO \end{matrix}\right. O$,	$O=Sn-Sn=O$ (with O bridging the two Sn);
or		
Stannous stannate, . . .	$SnOSno''$.	$O=Sn<^{O}_{O}>Sn$.

* With regard to the fusing points of alloys, or of any mixtures of fusible substances which do not chemically combine, the law holds that the fusing point of the mixture is lower than the main fusing point of the constituents in the proportion in which they are present.

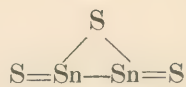
Metastannic acid (dried at 100° C.), ... $\left\{\begin{array}{l} \mathbf{Sn}Ho_3 \\ O \\ \mathbf{Sn}Ho_2 \\ O \\ \mathbf{Sn}O \\ O \\ \mathbf{Sn}Ho_2 \\ O \\ \mathbf{Sn}Ho_3 \end{array}\right.$.

Dipotassic metastannate, $\left\{\begin{array}{l} \mathbf{Sn}Ho_2Ko \\ O \\ \mathbf{Sn}Ho_2 \\ O \\ \mathbf{Sn}O \\ O \\ \mathbf{Sn}Ho_2 \\ O \\ \mathbf{Sn}Ho_2Ko \end{array}\right.$.

Stannous sulphide, . . . $\mathbf{Sn}S''$.

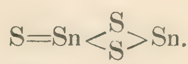
Stannic sulphide, . . . $\mathbf{Sn}S''_2$.

Distannic trisulphide, . . $\left\{\begin{array}{l} \mathbf{Sn}S'' \\ \mathbf{Sn}S'' \end{array}\right.S''$,

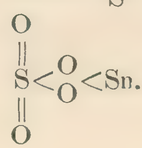


or

Stannous sulphostannate, . $\mathbf{Sn}S''Sns''$.



Stannous sulphate, . . . SO_2Sno''.



COMPOUNDS OF TIN WITH THE HALOGENS.

a. Stannous Compounds.

STANNOUS CHLORIDE.—*Up to* 700° C. $''\mathbf{Sn}''_2Cl_4$; *mol. wt.* = 378. *Between* 880° *and* 970° C. $\mathbf{Sn}Cl_2$*; *mol. wt.* = 189. *Fuses at* 250° C. (482° F.). *Boils about* 618° C. (1144.4° F.).

Preparation.—1. By heating a mixture of 1 part of tin-filings with 2 parts of mercuric chloride:

$$\underset{}{Sn} + \underset{\text{Mercuric chloride.}}{\mathbf{Hg}Cl_2} = \underset{\text{Stannous chloride.}}{\mathbf{Sn}Cl_2} + Hg.$$

* For the sake of greater simplicity in the formulæ, the smaller molecular formulæ have been employed for the stannous compounds.

The mercury distils off, and the stannous chloride remains as a vitreous mass, which may also be distilled at a higher temperature.

2. By dissolving tin in hydrochloric acid:

$$\mathrm{Sn} + \underset{\text{Hydrochloric acid.}}{2\mathrm{HCl}} = \underset{\text{Stannous chloride.}}{\mathbf{Sn}\mathrm{Cl}_2} + \mathrm{H}_2.$$

On evaporation of the aqueous solution, prismatic crystals of the formula $\mathbf{Sn}\mathrm{Cl}_2,2\mathbf{O}\mathrm{H}_2$, are obtained. The crystals dissolve in a small quantity of water, but a larger quantity decomposes them with formation of stannous oxydichloride and free hydrochloric acid:

$$\underset{\text{Stannous chloride.}}{2\mathbf{Sn}\mathrm{Cl}_2} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2} = \underset{\text{Stannous oxydichloride.}}{''\mathbf{Sn}''_2\mathrm{OCl}_2} + \underset{\text{Hydrochloric acid.}}{2\mathrm{HCl}}.$$

Stannous chloride readily unites with oxygen or chlorine, and hence acts as a powerful reducing agent. Mercury and gold are precipitated by it in the metallic state from solutions of their salts. The presence of an excess of hydrochloric acid prevents the separation of insoluble stannous oxydichloride during the reducing process:

$$\underset{\text{Mercuric oxide.}}{\mathbf{Hg}\mathrm{O}} + \underset{\text{Stannous chloride.}}{\mathbf{Sn}\mathrm{Cl}_2} + \underset{\text{Hydrochloric acid.}}{2\mathrm{HCl}} = \mathrm{Hg} + \underset{\text{Stannic chloride.}}{\mathbf{Sn}\mathrm{Cl}_4} + \underset{\text{Water.}}{\mathbf{O}\mathrm{H}_2}.$$

In like manner ferric, manganic, and cupric salts are reduced to ferrous, manganous, and cuprous salts. Chromic acid is converted into chromic oxide.

Stannous chloride is employed as a mordant in dyeing and calico-printing.

Stannous bromide, $\mathbf{Sn}\mathrm{Br}_2$, is obtained by dissolving tin in hydrobromic acid. It forms a grayish-white crystalline mass, readily soluble in water.

Stannous iodide, $\mathbf{Sn}\mathrm{I}_2$, may be prepared by acting upon finely divided tin with hydriodic acid, or by precipitating a concentrated solution of stannous chloride with potassic iodide. It crystallizes in sparingly soluble red needles, which are decomposed by an excess of water. It is volatile at a red heat.

Stannous fluoride, $\mathbf{Sn}\mathrm{F}_2$, is obtained in white lustrous monoclinic crystals by dissolving tin or stannous hydrate in hydrofluoric acid and evaporating the solution *in vacuo*.

b. Stannic Compounds.

STANNIC CHLORIDE, $\mathbf{Sn}\mathrm{Cl}_4$.—*Molecular weight* = 260. *Molecular volume* $\square\square$. *Sp. gr. of liquid* 2.267 *at* 0° C. *Boils at* 115° C. (239° F.). —This compound may be prepared either by the combustion of tin in a current of chlorine, or by heating a mixture of 1 part of tin-filings with 4 parts of mercuric chloride:

$$\mathrm{Sn} + \underset{\text{Mercuric chloride.}}{2\mathbf{Hg}\mathrm{Cl}_2} = \underset{\text{Stannic chloride.}}{\mathbf{Sn}\mathrm{Cl}_4} + 2\mathrm{Hg}.$$

The stannic chloride distils over, and is collected in the receiver.

Stannic chloride is a colorless mobile liquid, which fumes powerfully in contact with moist air. It unites with water, evolving great heat, and forming a crystalline aquate, $SnCl_4,3OH_2$. It dissolves in a small quantity of water, but an excess of water decomposes it, with formation of stannic and hydrochloric acids.

It unites with the soluble metallic chlorides to form *chlorostannates.* Ammonic chlorostannate $(NH_4)_2SnCl_6$ is the *pink salt* of the dyer.

Stannic chloride is also used in dyeing.

Stannic bromide, $SnBr_4$ (*molecular volume* $\square\square$), is obtained as a white, fusible crystalline mass by the direct union of tin and bromine. It fuses at 30° C. (86° F.), and boils at 201° C. (393.8° F.).

Stannic iodide, SnI_4, is prepared by heating together tin and iodine. It crystallizes in orange-colored octahedra, which fuse at 146° C. (294.8° F.). It boils at 295° C. (563° F.).

Stannic fluoride, SnF_4. The free compound has not been prepared. Numerous double fluorides of tetradic tin with other metals are, however, known: thus, *potassic stannicofluoride,* SnK_2F_6,OH_2; *sodic stannicofluoride,* $SnNa_2F_6$, and others. These stannicofluorides correspond with the silicofluorides (p. 316), with which they are, as a rule, isomorphous.

COMPOUNDS OF TIN WITH OXYGEN AND HYDROXYL.

a. Stannous Compounds.

STANNOUS OXIDE, SnO. *Molecular weight* = 134.—1. When stannous oxalate is heated to decomposition in a closed vessel, stannous oxide remains:

$$\underset{\substack{\text{Stannous}\\\text{oxalate.}}}{\left\{\begin{matrix}CO\\CO\end{matrix}\right.Sno''} = \underset{\substack{\text{Stannous}\\\text{oxide.}}}{SnO} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{CO.}$$

2. *Stannous hydrate,* $SnHo_2$, is obtained as a white precipitate by adding sodic carbonate to a solution of stannous chloride. It is converted into black stannous oxide by heating to 80° C. in an atmosphere of carbonic anhydride. If the stannous hydrate be boiled with a quantity of caustic alkali insufficient to dissolve it, the remaining hydrate is converted into small black shining crystals of the oxide (Fremy).

Stannous oxide is a black powder of sp. gr. 6.666. When heated in the air it becomes incandescent, and is converted into stannic oxide. With acids it yields the stannous salts.

b. Stannic Compounds.

STANNIC OXIDE or STANNIC ANHYDRIDE, SnO_2. *Molecular weight* = 150.—Stannic anhydride occurs in nature as tin-stone, crystallizing in forms belonging to the quadratic system. The crystals are generally dark-colored, owing to the presence of ferric and manganic oxides.

Stannic anhydride may be obtained artificially as a white, insoluble, amorphous powder by igniting stannic or metastannic acid. Amor-

phous stannic oxide assumes, on heating, a yellowish-brown color, which disappears on cooling. It may be obtained in quadratic crystals like those of native tin-stone, by heating it strongly in a current of gaseous hydrochloric acid.

Stannic anhydride is insoluble both in acids and in alkalies. It may even be fused with alkaline carbonates without undergoing change. By fusion with a caustic alkali it is rendered soluble, a stannate of the base being formed.

STANNIC ACID, $\mathbf{Sn}OHo_2$.—This acid is obtained as a colorless, gelatinous precipitate by decomposing a solution of stannic chloride with calcic carbonate, care being taken to avoid an excess of the precipitant:

$\mathbf{Sn}Cl_4$ +	$2\mathbf{CO}Cao''$ +	$\mathbf{O}H_2$ =	$\mathbf{Sn}OHo_2$ +	$2\mathbf{Ca}Cl_2$ +	$2\mathbf{CO}_2$.
Stannic chloride.	Calcic carbonate.	Water.	Stannic acid.	Calcic chloride.	Carbonic anhydride.

When dried *in vacuo* it has the composition expressed by the above formula.

It is soluble both in acids and in alkalies. With hydrochloric acid it yields a solution of stannic chloride. The stannic salts of the oxy-acids are very unstable. With bases it forms the *stannates*. The alkaline stannates crystallize well. Sodic stannate ($\mathbf{Sn}ONao_2,3\mathbf{O}H_2$) is employed in dyeing as a mordant, under the name of "preparing salt."

METASTANNIC ACID, $\mathbf{Sn}_5O_5Ho_{10}$.—This compound, which is polymeric with stannic acid, is prepared by oxidizing tin with nitric acid, and drying, at 100° C., the white powder ($\mathbf{Sn}_5O_5Ho_{10},5\mathbf{O}H_2$) thus obtained. By ignition it is converted into ordinary stannic anhydride.

Metastannic acid is insoluble in water. Hydrochloric acid combines with it without dissolving it, but the double compound thus formed is soluble in pure water, from which solution it is precipitated by boiling, or by the addition of concentrated hydrochloric acid. By prolonged digestion with concentrated hydrochloric acid, metastannic acid is converted into stannic chloride.

Metastannates.—Only two of the hydrogen atoms of metastannic acid are replaceable by bases. *Potassic metastannate*, $\mathbf{Sn}_5O_5Ho_8Ko_2$, is soluble in water, but insoluble in concentrated caustic potash.

It may be prepared by dissolving metastannic acid in cold caustic potash, and then adding solid caustic potash to the solution. It is gummy and uncrystallizable. The sodium salt, which may be obtained in a similar manner, forms crystalline granules.

DISTANNIC TRIOXIDE or STANNOUS STANNATE, $'\mathbf{Sn}'''_2O_3$ or $\mathbf{Sn}OSno''$.—The hydrate corresponding with this oxide is prepared by boiling a solution of stannous chloride with freshly precipitated ferric hydrate:

$2\mathbf{Sn}Cl_2$ +	$'\mathbf{Fe}'''_2Ho_6$ =	$'\mathbf{Sn}'''_2Ho_6$ (?) +	$2FeCl_2$.
Stannous chloride.	Ferric hydrate.	Distannic hexahydrate.	Ferrous chloride.

The hydrate forms a gray slimy precipitate, which, by heating in a current of carbonic anhydride, is converted into black distannic trioxide.

All the oxygen compounds of tin are reduced to the metallic state by ignition in a current of hydrogen or carbonic oxide, or by heating with charcoal.

COMPOUNDS OF TIN WITH SULPHUR.

Stannous sulphide, SnS'', may be prepared by heating together metallic tin and sulphur, when the two substances unite with incandescence. It forms a laminar crystalline mass of a bluish-gray color.

It may also be obtained as a dark brown precipitate by passing sulphuretted hydrogen into a solution of a stannous salt.

$$SnCl_2 + SH_2 = SnS'' + 2HCl.$$

$SnCl_2$	SH_2	SnS''	$2HCl$
Stannous chloride.	Sulphuretted hydrogen.	Stannous sulphide.	Hydrochloric acid.

Stannous sulphide dissolves in hot concentrated hydrochloric acid, yielding stannous chloride and sulphuretted hydrogen, by a reaction the reverse of the above.

It is soluble in a solution of an alkaline disulphide, forming a sulphostannate of the alkali:

$$SnS'' + \begin{cases} SK \\ SK \end{cases} = SnS''Ks_2.$$

SnS''	$\begin{cases} SK \\ SK \end{cases}$	$SnS''Ks_2$
Stannous sulphide	Dipotassic disulphide.	Potassic sulphostannate.

From this solution it is precipitated by acids as stannic, not as stannous, sulphide:

$$SnS''Ks_2 + 2HCl = SnS''_2 + 2KCl + SH_2.$$

$SnS''Ks_2$	$2HCl$	SnS''_2	$2KCl$	SH_2
Potassic sulphostannate.	Hydrochloric acid.	Stannic sulphide.	Potassic chloride.	Sulphuretted hydrogen.

Stannic sulphide, SnS''_2.—This compound cannot be prepared by merely heating tin and sulphur together. The addition of some volatile substance is necessary in order to lower the temperature during the reaction. An amalgam of 12 parts of tin and 6 parts of mercury is powdered, and heated with 7 parts of sulphur and 6 parts of ammonic chloride in a glass retort. Ammonic chloride, mercury, and sulphur, along with mercuric sulphide and mercurous chloride, volatilize, and the stannic sulphide remains in the flask as a mass of golden-yellow flakes with a metallic lustre. It is not certain whether the ammonic chloride takes part in the reaction or whether it acts merely by its volatilization.

Amorphous stannic sulphide is obtained as a brown precipitate by passing sulphuretted hydrogen into an acid solution of a stannic salt. After drying at ordinary temperatures, it still contains water of hydration, with which it parts on heating.

Amorphous stannic sulphide dissolves in hot concentrated hydrochloric acid, and the solution contains stannic chloride. Hot concentrated nitric acid also decomposes it. It is soluble in alkaline sulphides with formation of sulphostannates:

$$SnS''_2 + SK_2 = SnS''Ks_2;$$

SnS''_2	SK_2	$SnS''Ks_2$
Stannic sulphide.	Potassic sulphide.	Potassic sulphostannate.

and in caustic alkalies with formation of a mixture of stannate and sulphostannate:

$$\underset{\text{Stannic sulphide.}}{3\mathbf{Sn}S''_2} + \underset{\text{Potassic hydrate.}}{6\mathbf{O}KH} = \underset{\text{Potassic stannate.}}{\mathbf{Sn}OKo_2} + \underset{\text{Potassic sulphostannate.}}{2\mathbf{Sn}S''Ks_2} + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

Crystalline stannic sulphide is insoluble in all single acids, but soluble in aqua-regia. Alkalies and alkaline sulphides also dissolve it. Both the varieties of stannic sulphide are decomposed at a bright red heat into free sulphur and stannous sulphide.

Crystalline stannic sulphide is employed in the arts under the name of *mosaic gold* in the production of imitation bronze surfaces. It was known to the alchemists.

Sulphostannates.—Only the alkaline sulphostannates are soluble in water. Potassic sulphostannate is uncrystallizable. The sodium salt, $\mathbf{Sn}S''Nas_2,7\mathbf{O}H_2$, crystallizes in yellow regular octahedra.

Distannous trisulphide, or Stannous sulphostannate, $'\mathbf{Sn}'''_2S''_3$ or $\mathbf{Sn}S''Sns.''$—This compound is prepared by heating to low redness a mixture of 3 parts of stannous sulphide and 1 part of sulphur. It forms a grayish-yellow mass with a metallic lustre. When treated with hot concentrated hydrochloric acid, one half of the tin goes into solution as a stannous salt, the other half remaining behind as stannic sulphide. This reaction would seem to denote that the substance is not, as is frequently assumed, a distinct sulphide of tin, but a stannous sulphostannate.

All the sulphides of tin are reduced to the metallic state when heated to redness in a current of hydrogen.

General character and reactions of the salts of tin.—The *stannous salts*, when in solution, absorb oxygen from the air, and are converted into stannic salts. *Caustic alkalies* precipitate from the solutions white stannous hydrate, which is soluble in an excess of alkali. When an alkaline solution of stannous oxide is boiled, metallic tin separates out and an alkaline stannate remains in solution. *Ammonia* and the *alkaline carbonates* produce a precipitate of stannous hydrate, which is, however, not dissolved by an excess of the precipitant. With *sulphuretted hydrogen* in acid or neutral solutions, the whole of the tin is precipitated as brown stannous sulphide, almost insoluble in colorless ammonic sulphhydrate, readily soluble in yellow ammonic sulphide. In alkaline solutions of stannous salts the precipitate is either not formed at all or else the precipitation is incomplete. With a solution of *auric chloride* the stannous salts yield, if added in small quantity, a purple precipitate of aurostannous stannate ($\mathbf{Sn}_2O_2Auo_2$-$Sno'',4\mathbf{O}H_2$), known as *purple of Cassius;* an excess of the stannous salt produces a brown precipitate of metallic gold.

The *stannic salts* yield with *caustic alkalies* a white precipitate of stannic acid soluble in excess of alkali; and the solution gives no precipitate on boiling. With *sulphuretted hydrogen* a yellow precipitate of stannic sulphide is formed, soluble in alkalies and alkaline sulphides.

TITANIUM, Ti.

Atomic weight = 48. *Sp. gr.* 5.3. *Atomicity* '' *and* ^{iv}, *also a pseudo-triad.* *Evidence of atomicity*:

Titanous oxide, ...	$Ti''O$.
Titanic tetrachloride, ...	$Ti^{iv}Cl_4$.
Dititanic hexachloride, ...	$\left\{\begin{matrix} TiCl_3. \\ TiCl_3. \end{matrix}\right.$

History.—Titanium was discovered by Gregor in 1789.

Occurrence.—Titanium is one of the rarer elements. It is never found in the free state. As titanic anhydride ($\mathbf{Ti}O_2$) it occurs in three rare minerals—rutile, anatase, and brookite—and as ferrous titanate ($\mathbf{Ti}OFeo''$) in titaniferous iron ore.

Preparation.—1. Metallic titanium is most readily obtained by heating potassic titanofluoride with potassium in a covered crucible:

$$\underset{\text{Potassic titanofluoride.}}{TiK_2F_6} + 2K_2 = Ti + \underset{\text{Potassic fluoride.}}{6KF.}$$

On dissolving the product of the reaction in water the titanium remains as a gray amorphous powder.

2. It may also be obtained in the form of prismatic crystals by heating sodium in the vapor of titanic chloride:

$$\underset{\text{Titanic chloride.}}{\mathbf{Ti}Cl_4} + 2Na_2 = Ti + \underset{\text{Sodic chloride.}}{4NaCl.}$$

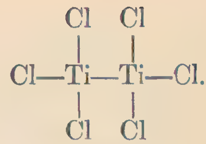
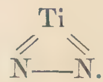
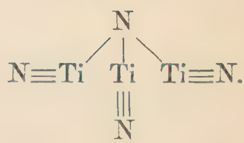
Properties.—Amorphous titanium forms a gray powder which, when heated in the air, or when thrown into a flame, burns with brilliant scintillations, forming titanic anhydride. At ordinary temperatures it does not decompose water, but at 100° C. hydrogen is evolved and titanic acid is formed:

$$Ti + \underset{\text{Water.}}{3\mathbf{O}H_2} = \underset{\text{Titanic acid.}}{\mathbf{Ti}OHo_2} + 2H_2.$$

It dissolves in hydrochloric and dilute sulphuric acids with evolution of hydrogen and formation of titanous salts.

The following are the names and probable formulæ of the chief compounds of titanium:

Titanic tetrachloride, ... $TiCl_4$. $\begin{matrix} & Cl & \\ & | & \\ Cl— & Ti & —Cl. \\ & | & \\ & Cl & \end{matrix}$

Dititanic hexachloride, ...	$\left\{ \begin{matrix} TiCl_3 \\ TiCl_3 \end{matrix} \right.$.	
Titanous oxide, ...	TiO.	Ti=O.
Titanic oxide or anhydride (Rutile, Anatase, Brookite), ...	TiO_2.	
Titanic acid, ...	$TiOHo_2$.	
Titanic sulphide, ...	TiS''_2.	
Titanic dinitride, ...	$'N''_2Ti$.	
Trititanic tetranitride, ...	$Ti_3N'''_4$.	

COMPOUNDS OF TITANIUM WITH CHLORINE.

Titanic Chloride, $TiCl_4$.

Molecular weight = 190. *Molecular volume* □□. *Sp. gr. of liquid* 1.76. *Boils at* 136° C. (276.8° F.).

This substance is prepared by heating a mixture of titanic anhydride and finely divided carbon in a current of chlorine:

$$\underset{\text{Titanic anhydride.}}{TiO_2} + 2C + 2Cl_2 = \underset{\text{Titanic chloride.}}{TiCl_4} + \underset{\text{Carbonic oxide.}}{2CO.}$$

It is a colorless strongly fuming liquid, which combines with a small quantity of water to form a crystalline compound, but is decomposed by an excess of water with separation of titanic acid.

Dititanic hexachloride, $\left\{ \begin{matrix} TiCl_3 \\ TiCl_3 \end{matrix} \right.$, is formed when a mixture of the vapor of the tetrachloride with dry hydrogen is passed through a red-hot tube:

$$\underset{\text{Titanic chloride.}}{2TiCl_4} + H_2 = \underset{\text{Dititanic hexachloride.}}{\left\{ \begin{matrix} TiCl_3 \\ TiCl_3 \end{matrix} \right.} + 2HCl.$$

It forms dark violet scales, which cannot be re-sublimed without decomposition. It is deliquescent, and dissolves in water to form a violet solution, which absorbs oxygen from the air, and becomes colorless.

COMPOUNDS OF TITANIUM WITH OXYGEN AND HYDROXYL.

Titanous oxide, TiO, has not been prepared in a state of purity. A hydrate, which has also not been isolated, is formed as a black precipitate when ammonia is added to the solution of a titanous salt prepared by dissolving titanium in a dilute acid. On boiling the liquid with the precipitate, the color of the latter changes to blue and ultimately to white, the oxide having been converted into titanic acid at the expense of the oxygen of the water, whilst hydrogen is evolved.

TITANIC OXIDE OR ANHYDRIDE, TiO_2.—The hydrate of this oxide, *tetrabasic titanic acid*, $TiHo_4$, is obtained as a white precipitate when ammonia is added to a solution of titanic chloride. This hydrate possesses both basic and acid properties, combining both with acids and with alkalies. When dried *in vacuo*, it parts with the elements of one molecule of water, and is converted into the acid $TiOHo_2$. At a higher temperature the rest of the water is eliminated, and *titanic anhydride* is left as a white amorphous powder, which on ignition becomes denser, and of a dark reddish-brown color. Titanic anhydride occurs in nature as *rutile*, crystallizing in reddish-brown quadratic prisms of sp. gr. 4.3; as *anatase* in quadratic pyramids, irreducible to the forms of rutile, and having a sp. gr. of 3.9; and as *brookite* in rhombic crystals of 4.1 sp. gr. Titanic anhydride is thus trimorphous. It may be obtained artificially in the same forms by passing a mixture of hydrochloric acid and steam over heated titanofluoride. At very high temperatures rutile is formed; at temperatures between the boiling-points of zinc and cadmium, crystals of brookite are deposited; whilst below the boiling-point of cadmium anatase is obtained. Titanic anhydride is insoluble in alkalies, and in all acids except hydrofluoric and hot concentrated sulphuric. The *titanates* have not been thoroughly investigated. All the normal titanates are insoluble in water.

Dititanic trioxide, Ti_2O_3, is obtained as a black powder by igniting titanic anhydride in a current of hydrogen. When heated strongly in air it is oxidized to titanic anhydride. Hydrochloric and nitric acids are without action upon it. Sulphuric acid dissolves it, yielding a violet solution.

COMPOUND OF TITANIUM WITH SULPHUR.

Titanic sulphide, TiS''_2, is formed when a mixture of the vapor of titanic chloride with dry sulphuretted hydrogen is passed through a red-hot tube:

$$\underset{\text{Titanic chloride.}}{TiCl_4} + \underset{\text{Sulphuretted hydrogen.}}{2SH_2} = \underset{\text{Titanic sulphide.}}{TiS''_2} + \underset{\text{Hydrochloric acid.}}{4HCl.}$$

It forms brass-yellow scales resembling mosaic gold. It burns when heated in the air, yielding titanic and sulphurous anhydrides. By exposure to moist air it is slowly decomposed, with evolution of sulphuretted hydrogen.

COMPOUNDS OF TITANIUM WITH NITROGEN AND WITH NITROGEN AND CARBON.

Titanic dinitride, $'N''_2Ti$, is obtained by heating titanic anhydride in a current of nitrogen:

$$TiO_2 + 2NH_3 = {'N''_2}Ti + 2OH_2 + H_2.$$

It is a dark violet-colored powder with a coppery tinge.

A second nitride, Ti_3N_4, *trititanic tetranitride,* is obtained in the form of a copper-colored metallic mass when the double compound of titanic chloride with ammonia ($TiCl_4,4NH_3$) is heated in a current of gaseous ammonia:

$$\underset{\text{Titanic chloride.}}{3TiCl_4} + \underset{\text{Ammonia.}}{4NH_3} = \underset{\text{Trititanic tetranitride.}}{Ti_3N_4} + \underset{\text{Hydrochloric acid.}}{12HCl.}$$

This compound was formerly mistaken for metallic titanium.

When trititanic tetranitride is strongly heated in a current of hydrogen, a third nitride, Ti_5N_6, *pentatitanic hexanitride,* is produced in the form of golden-yellow scales, with a strong metallic lustre.

All the nitrides of titanium, when heated with easily reducible oxides, such as those of copper, lead, and mercury, deflagrate brilliantly, the oxides undergoing reduction to the metallic state.

TITANIC CYANONITRIDE.—$Ti_5N_3(CN)$.—This remarkable compound, which was also formerly mistaken for metallic titanium, is frequently found in blast-furnaces which have been used for smelting titaniferous iron. It forms copper-colored metallic cubes, which are hard enough to scratch glass, and possess a sp. gr. of 5.3. The process by which this substance is formed may be imitated on a small scale by heating titanic anhydride, mixed with charcoal, in a current of nitrogen:

$$\underset{\text{Titanic anhydride.}}{5TiO_2} + 11C + 2N_2 = \underset{\text{Titanic cyanonitride.}}{Ti_5N_3(CN)} + \underset{\text{Carbonic oxide.}}{10CO.}$$

It is insoluble in acids. Heated in a current of steam it yields titanic anhydride, ammonia, and hydrocyanic acid. Heated in chlorine, titanic and cyanic chlorides are formed, whilst nitrogen is liberated.

GENERAL CHARACTER AND REACTIONS OF THE TITANIUM COMPOUNDS.—The *titanous salts* are unknown except in solution. With alkaline carbonates they yield a black precipitate, which becomes blue, and ultimately white.

The alkaline *titanates* are of a yellowish color. They are insoluble in water, but soluble in hydrochloric acid. On boiling the hydrochloric acid solution, white titanic acid is precipitated; ammonia produces the same effect. With microcosmic salt the titanates yield in the reducing flame of the blowpipe a violet glass which becomes colorless in the oxidizing flame.

ZIRCONIUM, Zr.

Atomic weight = 90. *Sp. gr.* 4.15. *Atomicity* ^{iv}. *Evidence of atomicity:*

Zirconic chloride, ... $ZrCl_4$.
Zirconic fluoride, ... ZrF_4.

Occurrence.—In combination with silicon and oxygen as zirconic silicate, it forms the rare mineral, *zircon,* $SiZro^{iv}$.

Preparation.—Zirconium is obtained by heating potassic zirconofluoride with potassium:

$$\underset{\text{Potassic zirconofluoride.}}{ZrK_2F_6} + 2K_2 = Zr + \underset{\text{Potassic fluoride.}}{6KF.}$$

On treating the mass with dilute hydrochloric acid the zirconium remains behind as a black amorphous powder. By employing alumin-

ium to reduce the potassic zirconofluoride the zirconium may be obtained in crystalline plates.

Reaction.—When heated in air, amorphous zirconium readily burns, forming zirconic oxide. The crystallized variety is oxidized only superficially, even at a white heat, but may be burnt with the aid of the oxyhydrogen blowpipe.

Zirconic chloride, $\mathbf{Zr}Cl_4$ (*molecular volume* $\square\square$), is prepared like titanic chloride (p. 331). It is a white crystalline mass, which, when treated with water, yields an oxychloride of the formula $\mathbf{Zr}OCl_2,8\mathbf{O}H_2$. *Zirconic bromide*, $\mathbf{Zr}Br_4$, is also known, and resembles the chloride in its properties and reactions.

Zirconic fluoride, $\mathbf{Zr}F_4$, is obtained by heating a mixture of zirconic oxide and fluorspar to whiteness in a current of gaseous hydrochloric acid:

$\mathbf{Zr}O_2$	+	$2\mathbf{Ca}F_2$	+	$4HCl$	=	$\mathbf{Zr}F_4$	+	$2\mathbf{Ca}Cl_2$	+	$2\mathbf{O}H_2$.
Zirconic oxide.		Calcic fluoride.		Hydrochloric acid.		Zirconic fluoride.		Calcic chloride.		Water.

It is a colorless crystalline transparent substance, volatile at a white heat, and soluble in a solution of hydrofluoric acid. With the fluorides of the metal it forms zirconofluorides, of which the most important is *potassic zirconofluoride*, $\mathrm{ZrK_2F_6}$.

Zirconic oxide, zirconia, $\mathbf{Zr}O_2$, is formed by burning zirconium in air, or by heating the hydrate. It is a white infusible powder. When heated in the oxyhydrogen blowpipe it emits a very intense light. Concentrated sulphuric acid dissolves it with difficulty. When fused with alkaline carbonates, it expels carbonic anhydride, and combines with the base to form a zirconate. On treating the fused mass with water, the zirconate is decomposed, and *zirconic hydrate*, $\mathbf{Zr}Ho_4$, separates out as a voluminous precipitate. The same precipitate is obtained by adding ammonia to the cold solution of a salt of zirconium. It dissolves readily in dilute acids. When ammonia is added to a hot solution of a zirconium salt a hydrate of the formula $\mathbf{Zr}OHo_2$ is precipitated. This second hydrate dissolves with difficulty in acids.

The method of fusing with an alkaline carbonate is employed in obtaining zirconia from its minerals.

THORIUM, Th.

Atomic weight = 233.4. *Sp. gr.* 11.23. *Atomicity* ^{iv}.

Occurrence.—This substance is of even rarer occurrence than zirconium. It is a constituent of the very rare minerals *thorite*, *monazite*, and *euxenite*.

Preparation.—It may be obtained as a dark gray powder by heating thoric chloride with potassium or sodium.

The following are some of its principal compounds:

Thoric chloride, ...	$\mathbf{Th}Cl_4$.
Thoric fluoride, ...	$\mathbf{Th}F_4,4\mathbf{O}H_2$.
Potassic thorofluoride, ...	$\mathrm{ThK_2F_6},2\mathbf{O}H_2$.
Thoric oxide, *thoria*, ...	$\mathbf{Th}O_2$.
Thoric silicate (*thorite*), ...	$\mathbf{Si}Tho^{iv},2\mathbf{O}H_2$.

CHAPTER XXX.

PENTAD ELEMENTS.

SECTION I. (*Continued from* Chapter XXVI.).

PHOSPHORUS, P_4.

Atomic weight = 31. *Molecular weight* = 124. *Molecular volume* $\square\square$. 1 *litre of phosphorus vapor weighs* 62 *criths. Sp. gr.* 1.83. *Fuses at* 44–45° C. (111–113° F.). *Boils at* 290° C. (554° F.). *Atomicity* $'''$, *and* ^{v}. *Evidence of atomicity:*

Phosphorous hydride,	$P'''H_3$.
Phosphorous chloride,	$P'''Cl_3$.
Phosphoric chloride,	$P^{v}Cl_5$.
Phosphonic iodide,	$P^{v}H_4I$.
Phosphoric fluoride,	$P^{v}F_5$.

History.—Phosphorus was discovered in 1669 by Brand, an alchemist of Hamburg, who obtained it by evaporating urine to dryness, and distilling the residue with sand. The process was kept secret; but in 1680 Boyle succeeded in preparing phosphorus, employing the same method. In 1769 Gahn showed that calcic phosphate is a constituent of bones, and in 1771 Scheele published a method of obtaining phosphorus from this source.

Occurrence.—Phosphorus is never found in the free state in nature. It generally occurs combined with oxygen and a metal to form a phosphate. The principal naturally occurring phosphates are *osteolite* (*estramadurite, sombrerite*) or *calcic phosphate*, $\begin{matrix}PO\\PO\end{matrix}Cao''_3$, and *apatite* or *calcic chlorophosphate*, $(PO)'''_3Cao''_4(OCaCl)$. Calcic phosphate is widely distributed in small quantities as a constituent of the primitive rocks, by the disintegration of which it passes into the soil. From the soil the phosphorus is absorbed by plants, where it accumulates chiefly in the seed. From plants it passes into the bodies of animals, in which it is found in still greater quantity. Calcic phosphate forms the chief inorganic constituent of the bones, whilst phosphorus in complex organic combinations is always present in the substance of the nerves and brain, and in smaller quantity in the other tissues. In the slow oxidation of the living animal substance which is constantly going on, the phosphorus is eliminated in the urine as phosphates of sodium, potassium, and magnesium.

Preparation.—1. Calcined bones, which consist of calcic phosphate with a slight admixture of calcic carbonate, are digested with sufficient sulphuric acid to decompose the whole of the carbonate and two-thirds of the phosphate. In this way the tricalcic diphosphate is converted into tetrahydric calcic diphosphate:

$$\underset{\text{Tricalcic diphosphate (Bone-ash).}}{P_2O_2Cao''_3} + \underset{\text{Sulphuric acid.}}{2SO_2Ho_2} = \underset{\text{Tetrahydric calcic diphosphate.}}{P_2O_2Ho_4Cao''} + \underset{\text{Calcic sulphate.}}{2SO_2Cao''}.$$

The tetrahydric calcic diphosphate is extracted with water from the calcic sulphate, evaporated to a syrup, mixed with charcoal, and heated to dull redness in an iron pot, stirring all the time. Under the influence of heat the tetrahydric calcic diphosphate parts with water, and is converted into calcic metaphosphate, which is thus obtained intimately mixed with charcoal:

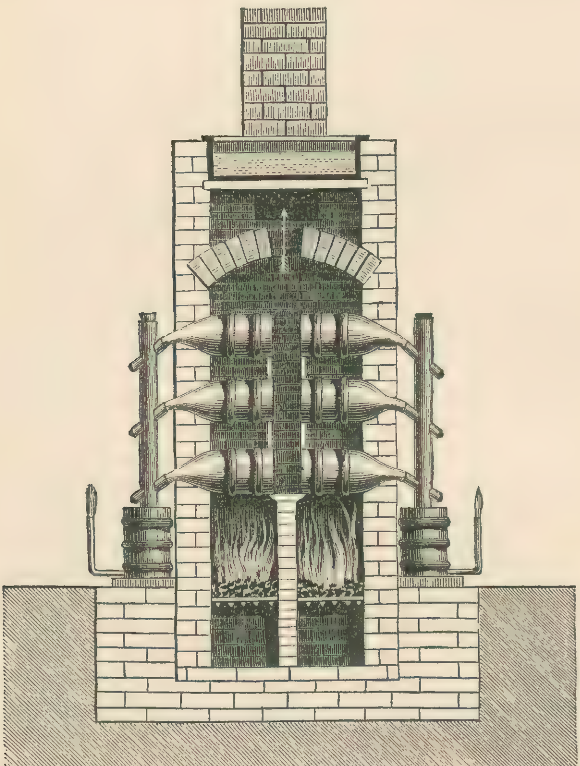
$$\underset{\text{Tetrahydric calcic diphosphate.}}{\mathbf{P}_2\mathrm{O}_2\mathrm{Ho}_4\mathrm{Cao}''} = \underset{\text{Calcic metaphosphate.}}{\mathbf{P}_2\mathrm{O}_4\mathrm{Cao}''} + \underset{\text{Water.}}{2\mathbf{O}\mathrm{H}_2}.$$

The mixture is then transferred to earthenware retorts and heated to bright redness, when the following reaction takes place:

$$\underset{\text{Calcic metaphosphate.}}{3\mathbf{P}_2\mathrm{O}_4\mathrm{Cao}''} + 10\mathrm{C} = \underset{\text{Tricalcic diphosphate.}}{\mathbf{P}_2\mathrm{O}_2\mathrm{Cao}''_3} + \underset{\text{Carbonic oxide.}}{10\mathbf{C}\mathrm{O}} + \mathrm{P}_4.$$

The phosphorus distils over, and is collected under water, whilst the carbonic oxide escapes carrying with it a small quantity of phosphorus

Fig. 46.



vapor, which causes it to inflame on coming in contact with the air. The apparatus employed in this distillation varies in different factories; one form is shown in Fig. 46.

The explanation of the process is as follows: Normal salts of tribasic phosphoric acid are not acted upon when heated with charcoal, but phosphoric anhydride, under these circumstances, is readily reduced. If we regard a salt as a compound of anhydride and base, it will be seen that the salts of monobasic phosphoric acid contain more anhydride in proportion than the tribasic acid. Thus:

$$3P_2O_4Cao'' = P_2O_2Cao''_3 + 2P_2O_5.$$

The reduction takes place to the extent of the excess of anhydride above what is necessary for the formation of tricalcic diphosphate. Accordingly, in the above process two-thirds of the phosphorus present are reduced.

Sombrerite, an impure calcic phosphate found in the West Indies, is frequently substituted for bone-ash.

2. If sand be added to the mixture in the above distillation, calcic silicate is formed, and the whole of the phosphorus is expelled (Wöhler):

$$\underset{\text{Calcic metaphosphate.}}{2P_2O_4Cao''} + 10C + \underset{\text{Silicic anhydride.}}{2SiO_2} = \underset{\text{Calcic silicate.}}{2SiOCao''} + \underset{\text{Carbonic oxide.}}{10CO} + P_4.$$

3. If a mixture of bone-ash and charcoal be heated to redness in a current of gaseous hydrochloric acid, the whole of the phosphorus is liberated, and calcic chloride remains (Cary-Montrand):

$$\underset{\text{Tricalcic diphosphate.}}{P_2O_2Cao''_3} + C_8 + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Calcic chloride.}}{3CaCl_2} + \underset{\text{Carbonic oxide.}}{8CO} + 3H_2 + P_2.$$

This process has not, however, proved successful on a manufacturing scale.

The crude phosphorus is always contaminated by particles of charcoal and other impurities carried over during the distillation. From these it is freed, either by fusing it under water and pressing it through wash-leather bags, or by partially oxidizing it with a mixture of potassic dichromate and sulphuric acid. The oxidation is attended with effervescence, which causes the impurities to rise to the surface, leaving the phosphorus pure. The purified phosphorus is cast into sticks.

Properties.—Phosphorus exists in several allotropic modifications.

Common or *octahedral phosphorus*, the modification obtained in the processes above described, is, when freshly prepared, a colorless transparent solid. Very frequently, however, it displays a faint yellowish tinge due to the presence of some impurity. It has a sp. gr. of 1.83. It is a non-conductor of electricity. At ordinary temperatures it may be cut with a knife like wax, but about 0° C. it becomes brittle. At a temperature of 44–45° C. (111–113° F.) it fuses to a colorless oily liquid, which readily retains its fluidity several degrees below its solidifying point. It boils at 290° C. (554° F.). The molecular weight of phosphorus, deduced from the vapor-density, is 124, showing that

the molecule of phosphorus consists of *four* atoms, and this tetratomic molecule does not break up even at a temperature of 1040° C. (1840° F.) (Deville and Troost); but at a higher temperature, the vapor-density has a value lying between the values required for P_2 and P_4 respectively, showing that a partial dissociation has taken place (Victor Meyer).

Phosphorus is a very inflammable substance, igniting in the air a few degrees above its fusing-point. For this reason it must always be preserved and cut under water. Under the influence of air and light it becomes covered, when kept under water, with a white opaque crust, due to a partial oxidation. It ought therefore to be kept in the dark.

When exposed to the air at ordinary temperatures phosphorus undergoes slow oxidation, and gives off a white vapor, which has a powerful odor of garlic. In a dark room both the phosphorus and the vapor are luminous with a greenish-white light. At a few degrees below 0° C. the oxidation and the luminosity cease. In pure oxygen under ordinary pressures phosphorus is not luminous at temperatures below 15° C.; but by rarefying the oxygen, or adding some inactive diluent, such as nitrogen, hydrogen, or carbonic anhydride, the phosphorus again becomes luminous. The luminosity of phosphorus in air is also prevented by the presence of minute traces of certain gases or vapors, such as olefiant gas, sulphuretted hydrogen, and turpentine.* When phosphorus is exposed to the air in large quantities, the heat of oxidation is frequently sufficient to melt, and finally to ignite, the mass. The same effect is produced by exposing phosphorus to the air in a finely divided condition, so as to increase the oxidizable surface. This may be shown by pouring a solution of phosphorus in carbonic disulphide upon filtering paper, and allowing the liquid to evaporate. In the dark the paper becomes brightly luminous, and at last bursts into flame.

Phosphorus is insoluble in water, slightly soluble in ether, turpentine, and benzine, readily soluble in disulphur dichloride, phosphorous chloride, and carbonic disulphide. One part by weight of the latter solvent dissolves from seventeen to eighteen parts of phosphorus. By the spontaneous evaporation of this solution it may be obtained in transparent crystals belonging to the regular system, generally octahedra or rhombic dodecahedra. When phosphorus is kept in the dark in sealed vacuous tubes, it spontaneously sublimes, and is deposited on the sides of the tubes in very lustrous and perfect crystals.

Phosphorus may be finely granulated by melting it under water, and agitating until it solidifies again. The addition of a small quantity of urea to the water prevents the adhesion of the granules, and by this means a higher degree of subdivision is attained.

Phosphorus is an exceedingly poisonous substance. Even the fumes have a very deleterious action when inhaled, producing caries of the bones of the jaw.

Red or Amorphous Phosphorus.—This variety was discovered by Schrötter in 1845. It is formed when ordinary phosphorus is exposed

* According to Chappuis, the luminosity of phosphorus depends upon the presence of ozone. Substances which destroy ozone prevent the luminosity.

to the action of the heat or light in an atmosphere devoid of oxygen. It is best prepared by heating phosphorus for some time in a closed vessel to 230–250° C. (446–482° F.). On a manufacturing scale, iron vessels are employed for this purpose, and it is not necessary to fill the apparatus with any artificial atmosphere, as the oxygen is speedily removed from the air by the combustion of a small portion of the phosphorus. Any rise of temperature above 250° C. must be carefully avoided, since at 260° C. (500° F.) amorphous phosphorus is reconverted into the ordinary modification, the change being accompanied with evolution of heat and taking place, in the case of large quantities, with explosive violence. Amorphous phosphorus is, however, formed when ordinary phosphorus is heated under pressure in closed iron vessels to 300° C. (572° F.), the change taking place in a few minutes.

When ordinary phosphorus is heated with a small quantity of iodine or selenium, an iodide or selenide is formed, and the excess of phosphorus is instantaneously converted into the red variety.

Amorphous phosphorus, prepared by any of the above methods, invariably contains a small quantity of white phosphorus, the presence of which renders the product dangerously inflammable. From this it may be freed by grinding the crude amorphous phosphorus under water, and subsequently treating it with carbonic disulphide, which dissolves the unaltered phosphorus, or still more advantageously by boiling with caustic soda (see *Phosphoretted Hydrogen*). Thus purified, amorphous phosphorus forms a reddish-brown powder of sp. gr. 2.15. It is devoid of taste and smell, is not poisonous, may be exposed to the air for any length of time without undergoing change, and is not luminous in the dark. When heated it does not fuse, and inflames in the air only at a temperature of 260° C. (500° F.), being converted at the same time into ordinary phosphorus. It is insoluble in the solvents which dissolve ordinary phosphorus, such as carbonic disulphide and sulphur chloride. It conducts electricity feebly.

Rhombohedral Phosphorus.—This variety is obtained when phosphorus is heated with metallic lead in sealed tubes for eight or nine hours to a temperature below redness. On dissolving the cooled lead in dilute nitric acid, small, well-defined, violet-black rhombohedra, having a sp. gr. of 2.34, remain. This modification may also be obtained by heating amorphous phosphorus under pressure to 580° C. (1076° F.).

According to some chemists red phosphorus and rhombohedral phosphorus are identical.

A fourth modification, obtained as a black mass by quickly cooling melted phosphorus, has been described; but it has been shown that this substance is produced only when metals are present, the color being due to the formation of metallic phosphides.

Reactions.—Owing to its affinity for oxygen, phosphorus acts as a powerful reducing agent. Platinum, gold, silver, and copper are deposited in the metallic state, when white phosphorus is left in contact with the solutions of their salts. When sodic carbonate is heated to redness with phosphorus, the carbonic anhydride is reduced and carbon is set free. When dry finely divided phosphorus is mixed with

substances which readily part with oxygen, such as potassic chlorate or metallic peroxides, very slight friction is sufficient to cause the explosive oxidation of the phosphorus.

The other reactions of phosphorus will be described in connection with its compounds.

Uses.—Phosphorus is employed chiefly in the manufacture of lucifer matches. In the commoner sorts, the matches are tipped first with sulphur, and then with a mixture of phosphorus and potassic chlorate made into a paste with glue. They ignite by friction on any rough surface. The sulphur serves to transmit the combustion from the phosphorus to the wood. Nitre is frequently substituted for potassic chlorate, as the matches thus prepared ignite more quietly; whilst, in order to get rid of the disagreeable smell of burning sulphur, this substance is replaced by paraffin. In the *safety matches* the phosphorus is separated from the other inflammable materials. The matches are tipped with a mixture of potassic chlorate, potassic dichromate, red lead, and antimonious sulphide, and are ignited by friction on a prepared surface coated with amorphous phosphorus and antimonious sulphide. These matches do not readily ignite on an unprepared surface, but by rubbing them rapidly over a smooth slate, or a sheet of ground glass, they may be inflamed.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

Phosphorus forms with hydrogen three compounds. These cannot be obtained by the direct combination of their elements.

Solid phosphoretted hydrogen,		. . . .	$\left\{\begin{array}{l}\mathbf{P}(\mathrm{P}'''\mathrm{H})'' \\ \mathbf{P}(\mathrm{P}'''\mathrm{H})''\end{array}\right.$
Liquid	"	"	$'\mathbf{P}''_2\mathrm{H}_4$.
Gaseous	"	"	$\mathbf{P}\mathrm{H}_3$.

GASEOUS PHOSHPORETTED HYDROGEN.

Phosphine.

$$\mathbf{P}\mathrm{H}_3. \qquad \begin{array}{c}\mathrm{H} \\ | \\ \mathrm{H—P—H}\end{array}$$

Molecular weight = 34. *Molecular volume* $\square\square$. 1 *litre weighs* 17 *criths.*

Preparation.—1. Phosphoretted hydrogen may be obtained by heating hypophosphorous acid:

$$\underset{\text{Hypophosphorous acid.}}{2\mathbf{P}\mathrm{HHo}_2} = \underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}\mathrm{H}_3} + \underset{\text{Phosphoric acid.}}{\mathbf{P}\mathrm{OHo}_3}.$$

2. A similar decomposition occurs when phosphorous acid is heated:

$$\underset{\text{Phosphorous acid.}}{4PHo_3} = \underset{\text{Phosphoretted hydrogen.}}{PH_3} + \underset{\text{Phosphoric acid.}}{3POHo_3}.$$

3. When phosphorus is heated with a solution of sodic or potassic hydrate, phosphoretted hydrogen is evolved, whilst an alkaline hypophosphite remains in the retort:

$$\underset{\text{Sodic hydrate.}}{3ONaH} + P_4 + \underset{\text{Water.}}{3OH_2} = \underset{\text{Sodic hypophosphite.}}{3PHHoNao} + \underset{\text{Phosphoretted hydrogen.}}{PH_3}.$$

The gas prepared by this process contains free hydrogen and liquid phosphoretted hydrogen, the presence of this latter substance rendering the gas spontaneously inflammable in contact with air. By employing an alcoholic solution of caustic alkali, a gas is obtained which does not inflame spontaneously, the liquid phosphoretted hydrogen remaining in this case dissolved in the alcohol.

4. Phosphoretted hydrogen is evolved when calcic phosphide is treated with water:

$$\underset{\text{Tricalcic diphosphide.}}{P_2Ca_3} + \underset{\text{Water.}}{6OH_2} = \underset{\text{Phosphoretted hydrogen.}}{2PH_3} + \underset{\text{Calcic hydrate.}}{3CaHo_2}.$$

The gas is also in this case contaminated with the vapor of liquid phosphoretted hydrogen.

5. Pure phosphoretted hydrogen is most readily obtained by allowing concentrated caustic potash to drop very gradually upon phosphonic iodide (*q.v.*) contained in a flask:

$$\underset{\text{Phosphonic iodide.}}{PH_4I} + \underset{\text{Potassic hydrate.}}{OKH} = \underset{\text{Phosphoretted hydrogen.}}{PH_3} + \underset{\text{Potassic iodide.}}{KI} + \underset{\text{Water.}}{OH_2}.$$

Properties—Phosphoretted hydrogen is a colorless gas possessing an odor resembling that of garlic. It is combustible in air or oxygen, burning with a very brilliant white light, and evolving a cloud of phosphoric acid. When pure it is not spontaneously inflammable; but the presence of a small quantity of the vapor of liquid phosphoretted hydrogen ($'P''_2H_4$) in the gas suffices to impart to it this property, of which it may again be deprived by leaving it in contact with finely divided charcoal, which absorbs the liquid compound, or by exposing it to the action of sunlight, by which the liquid compound is decomposed. On the other hand, the pure gas may be rendered spontaneously inflammable by the addition of a trace of nitrous anhydride.

If the pure gas be mixed with oxygen no action is observed; but, on suddenly rarefying the mixture, combination takes place with explosion. This phenomenon is possibly allied to that of the luminosity of phosphorus in rarefied oxygen.

If the spontaneously inflammable gas be allowed to bubble through

water, each bubble, on escaping into the air and inflaming, forms a smoke-ring of phosphoric acid.

Phosphoretted hydrogen is a highly poisonous gas. When inhaled, even in a very diluted condition, it produces difficulty in breathing, and ultimately death.

Reactions.—1. By combustion in oxygen it yields metaphosphoric acid and water:

$$\underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}H_3} + 2O_2 = \underset{\text{Metaphosphoric acid.}}{\mathbf{P}O_2Ho} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

2. In contact with chlorine it forms phosphoric chloride and hydrochloric acid:

$$\underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}H_3} + 4Cl_2 = \underset{\text{Phosphoric chloride.}}{\mathbf{P}Cl_5} + \underset{\text{Hydrochloric acid.}}{3HCl}.$$

3. When passed through a solution of cupric sulphate, it produces a black precipitate of cupric phosphide:

$$\underset{\text{Phosphoretted hydrogen.}}{2\mathbf{P}H_3} + \underset{\text{Cupric sulphate.}}{3\mathbf{S}O_2Cuo''} = \underset{\text{Cupric phosphide.}}{\mathbf{P}_2Cu''_3} + \underset{\text{Sulphuric acid.}}{3\mathbf{S}O_2Ho_2}.$$

4. When passed through a solution of argentic nitrate, metallic silver is deposited, whilst nitric and phosphoric acids are formed:

$$\underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}H_3} + \underset{\text{Argentic nitrate.}}{8\mathbf{N}O_2Ago} + \underset{\text{Water.}}{4\mathbf{O}H_2} = \underset{\text{Phosphoric acid.}}{\mathbf{P}OHo_3}$$
$$+ 4Ag_2 + \underset{\text{Nitric acid.}}{8\mathbf{N}O_2Ho}.$$

5. It unites directly with hydrochloric, hydrobromic, and hydriodic acids, when the dry gases are brought together, forming compounds analogous to the haloid salts of ammonium:

$$\underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}H_3} + \underset{\text{Hydrobromic acid.}}{HBr} = \underset{\text{Phosphonic bromide.}}{\mathbf{P}H_4Br}.$$

Phosphoretted hydrogen and hydrochloric acid unite only under the influence of pressure and cold (Ogier).

Phosphonic iodide is also formed by the action of iodine on phosphoretted hydrogen. The reaction takes place in two stages:

$$\underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}H_3} + 3I_2 = \underset{\text{Phosphorus iodide.}}{\mathbf{P}I_3} + \underset{\text{Hydriodic acid.}}{3HI};$$

and

$$\underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}H_3} + \underset{\text{Hydriodic acid.}}{HI} = \underset{\text{Phosphonic iodide.}}{\mathbf{P}H_4I}.$$

Phosphonic iodide is, however, most conveniently prepared by the following method (A. W. Hofmann): 10 parts of phosphorus are dis-

solved in carbonic disulphide in a retort, and 17 parts of iodine are gradually added, cooling during the operation. The carbonic disulphide is then distilled off, a stream of dry carbonic anhydride being finally passed through the apparatus to remove the last traces of the carbonic disulphide, and 6 parts of water are very slowly added by means of a dropping-funnel. A violent reaction takes place, the heat of which volatilizes the phosphonic iodide as it is formed. Towards the close heat is applied to the retort. A slow stream of carbonic anhydride must be passed through the apparatus during the whole operation, in order to prevent the entrance of air, which might otherwise occasion an explosion. The phosphonic iodide condenses in large lustrous quadratic crystals in a wide tube attached to the neck of the retort.

The following equation expresses the reaction:

$$13P + 9I + \underset{\text{Water.}}{21\mathbf{O}H_2} = \underset{\substack{\text{Phosphonic}\\ \text{iodide.}}}{7PH_4I} + \underset{\substack{\text{Hydriodic}\\ \text{acid.}}}{2HI} + \underset{\substack{\text{Pyrophosphoric}\\ \text{acid.}}}{3\mathbf{P}_2O_3Ho_4}.$$

Phosphonic iodide is employed in the laboratory as a powerful reducing agent, available particularly at high temperatures.

Composition.—When a series of electric sparks is passed through phosphoretted hydrogen, it is gradually decomposed into its elements. The spark should pass between carbon points, since, when platinum is employed, a fusible phosphide of platinum is formed, which melts, putting an end to the experiment. It is found that two volumes of phosphoretted hydrogen yield three volumes of hydrogen when thus treated. Expressed in litres:

2 litres of phosphoretted hydrogen weigh . . .	34 criths.
Deduct weight of 3 litres of hydrogen, . . .	3 "
There remain, ...	31 "

which is the weight of $\frac{1}{2}$ litre of phosphorus vapor. Therefore $\frac{1}{2}$ volume of phosphorus vapor in combination with 3 volumes of hydrogen yields 2 volumes of phosphoretted hydrogen, or 31 parts by weight of phosphorus combine with 3 parts by weight of hydrogen to form this compound, and its formula is, therefore, $\mathbf{P}H_3$.

LIQUID PHOSPHORETTED HYDROGEN.

$$'\mathbf{P}''_2H_4 \text{ or } \left\{\begin{array}{l}\mathbf{P}H_2\\ \mathbf{P}H_2\end{array}\right. . \qquad \begin{array}{ccc} H & & H \\ | & & | \\ P & — & P \\ | & & | \\ H & & H \end{array}$$

Molecular weight = 66. *Molecular volume* $\square\square$. 1 *litre of the vapor weighs* 33 *criths.*

Preparation.—This compound is formed along with gaseous phosphoretted hydrogen by the action of water at a temperature of 60–70°

C. (140–158° F.) on calcic phosphide obtained by passing the vapor of phosphorus over lime heated to redness (see *Calcic Phosphide*). This latter substance probably contains, in addition to calcic pyrophosphate, a mixture of dicalcic ($'\mathbf{P}''_2Ca''_2$) and tricalcic diphosphide ($\mathbf{P}_2Ca''_3$), and from these two phosphides the liquid and gaseous phosphoretted hydrogens are respectively formed:

$$\underset{\text{Dicalcic diphosphide.}}{'\mathbf{P}''_2Ca''_2} + \underset{\text{Water.}}{4OH_2} = \underset{\text{Liquid phosphoretted hydrogen.}}{'\mathbf{P}''_2H_4} + \underset{\text{Calcic hydrate.}}{2CaHo_2}.$$

(For the formation of gaseous phosphoretted hydrogen from tricalcic diphosphide, see p. 341.) The gas evolved is passed through a U-tube immersed in a freezing mixture, and in this the liquid compound condenses.

Properties.—It is a colorless, powerfully refracting liquid which inflames instantly in contact with air.

Reaction.—By exposure to sunlight, or by contact with hydrochloric acid, it is decomposed into solid and gaseous phosphoretted hydrogens:

$$\underset{\text{Liquid phosphoretted hydrogen.}}{5'\mathbf{P}''_2H_4} = \underset{\text{Gaseous phosphoretted hydrogen.}}{6\mathbf{P}H_3} + \underset{\text{Solid phosphoretted hydrogen.}}{\left\{\begin{matrix}\mathbf{P}(P'''H)'' \\ \mathbf{P}(P'''H)''\end{matrix}\right.?}$$

The hydrochloric acid suffers no change. A very small quantity of the acid therefore suffices to decompose a practically unlimited quantity of the phosphorus compound.

SOLID PHOSPHORETTED HYDROGEN.

$$\left\{\begin{matrix}\mathbf{P}(P'''H)'' \\ \mathbf{P}(P'''H)''\end{matrix}\right.?$$

Molecular weight = 126 ?

Preparation.—Solid phosphoretted hydrogen is obtained by dissolving calcic phosphide in concentrated hydrochloric acid, or by the action of light upon the liquid phosphoretted hydrogen.

Properties.—It forms a yellow powder which turns darker on exposure to light. When strongly heated in an atmosphere of carbonic avhydride, it is decomposed into its elements. It is doubtful whether this substance has ever been prepared in a state of purity, and its exact composition is uncertain.

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

Phosphorous chloride, ...	$\mathbf{P}Cl_3$.
Phosphoric chloride, ...	$\mathbf{P}Cl_5$.
Phosphorous bromide, ...	$\mathbf{P}Br_3$.
Phosphoric bromide, ...	$\mathbf{P}Br_5$.
Diphosphorous tetriodide, ...	$\left\{\begin{matrix}\mathbf{P}I_2 \\ \mathbf{P}I_2\end{matrix}\right.$.
Phosphorous iodide, ...	$\mathbf{P}I_3$.
Phosphoric fluoride, ...	$\mathbf{P}F_5$.

PHOSPHOROUS CHLORIDE.

$$\mathbf{PCl_3}. \qquad \begin{array}{c} Cl \\ | \\ Cl—P—Cl \end{array}$$

Molecular weight = 137.5. *Molecular volume* $\square\square$. 1 *litre of phosphorous trichloride vapor weighs* 68.75 *criths. Sp. gr.* 1.613. *Boils at* 76° C. (168.8° F.).

Preparation.—This compound is obtained by heating amorphous phosphorus in a retort while a current of dry chlorine is passed over it through the tubulure. The phosphorous chloride distils off as fast as it is formed, and collects in a cooled receiver. In order to free it from pentachloride, it is redistilled over ordinary phosphorus.

Properties.—Phosphorous chloride is a colorless fuming liquid with a very pungent odor. It does not solidify at —115° C. (—175° F.).

Reactions.—1. With water it yields hydrochloric and phosphorous acids:

$\mathbf{PCl_3}$	+	$3OH_2$	=	$3HCl$	+	$\mathbf{PHo_3}$.
Phosphorous chloride.		Water.		Hydrochloric acid.		Phosphorous acid.

2. With sulphuretted hydrogen it forms hydrochloric acid and phosphorous sulphide:

$\mathbf{2PCl_3}$	+	$\mathbf{3SH_2}$	=	$6HCl$	+	$\mathbf{P_2S''_3}$.
Phosphorous chloride.		Sulphuretted hydrogen.		Hydrochloric acid.		Phosphorous sulphide.

PHOSPHORIC CHLORIDE.

$$\mathbf{PCl_5}. \qquad \begin{array}{c} Cl \\ | \\ Cl—P—Cl \\ / \quad \backslash \\ Cl \quad Cl \end{array}$$

Molecular weight = 208.5. *Molecular volume* $\square\square$. 1 *litre of undissociated phosphoric chloride vapor weighs* 104.25 *criths. Volatilizes below* 100° C.

Preparation.—Phosphoric chloride is formed by the direct union of the trichloride with chlorine. A stream of dry chlorine is passed on to the surface of the trichloride contained in a flask cooled by water. Great heat is evolved in the reaction. The liquid ultimately solidifies to a crystalline mass.

Properties.—Phosphoric chloride is a crystalline powder with a faint yellowish tinge. It fumes in contact with moist air, and possesses a

very irritating odor. It sublimes readily, but cannot be fused under ordinary pressure. In a sealed tube, under the pressure of its own vapor, it fuses at 148° C. (298.4° F.), and on cooling, solidifies in prismatic crystals. At higher temperatures it possesses a vapor-density only half as great as is required for the molecular weight corresponding to the formula PCl_5, the reason of this being that the compound undergoes dissociation into PCl_3 and Cl_2 (Introduction, p. 64). This dissociation is only partial at lower temperatures, and its progress may be traced by means of the change of color which the vapor undergoes as the temperature rises, phosphoric chloride yielding a colorless vapor which becomes yellowish-green as the proportion of free chlorine increases. This dissociation is to a great extent checked by allowing the phosphoric chloride to volatilize in an atmosphere of phosphorous chloride vapor, and in this way Wurtz determined the vapor-density of phosphoric chloride with a result closely agreeing with the normal density required for the formula PCl_5.

Reactions.—1. A small quantity of water converts it into phosphoric oxytrichloride with formation of hydrochloric acid:

PCl_5	+	OH_2	=	$POCl_3$	+	$2HCl$.
Phosphoric chloride.		Water.		Phosphoric oxytrichloride.		Hydrochloric acid.

2. With an excess of water, it yields phosphoric and hydrochloric acids:

PCl_5	+	$4OH_2$	=	$POHo_3$	+	$5HCl$.
Phosphoric chloride.		Water.		Phosphoric acid.		Hydrochloric acid.

3. By its action on alcohols and acids, the chlorides of the radicals of the alcohols and acids are obtained, thus:

$\left\{\begin{array}{l} CH_3 \\ CH_2Ho \end{array}\right.$	+	PCl_5	=	$\left\{\begin{array}{l} CH_3 \\ CH_2Cl \end{array}\right.$	+	HCl	+	$POCl_3$.
Ethylic alcohol.		Phosphoric chloride.		Ethylic chloride.		Hydrochloric acid.		Phosphoric oxytrichloride.

$\left\{\begin{array}{l} CH_3 \\ COHo \end{array}\right.$	+	PCl_5	=	$\left\{\begin{array}{l} CH_3 \\ COCl \end{array}\right.$	+	HCl	+	$POCl_3$.
Acetic acid.		Phosphoric chloride.		Acetylic chloride.		Hydrochloric acid.		Phosphoric oxytrichloride.

4. When phosphoric chloride acts on organic compounds containing oxygen attached with both its bonds to the same atom of carbon, a direct exchange of one atom of oxygen for two atoms of chlorine is effected:

$\left\{\begin{array}{l} C_6H_5 \\ COH \end{array}\right.$	+	PCl_5	=	$\left\{\begin{array}{l} C_6H_5 \\ CCl_2H \end{array}\right.$	+	$POCl_3$.
Benzaldehyde.		Phosphoric chloride.		Benzalchloride.		Phosphoric oxytrichloride.

These properties render phosphoric chloride an invaluable agent in the investigation of organic compounds.

Phosphorous bromide, PBr_3 (*molecular volume* □□), is prepared by the action of bromine on amorphous phosphorus. It forms a fuming colorless liquid of sp. gr. 2.925 at 0° C., boiling at 175° C. (347° F.). Its chemical behavior is analogous to that of the chloride.

Phosphoric bromide, PBr_5, is obtained by the direct union of the tribromide with bromine. It is a yellow crystalline solid which melts to a red liquid, and is decomposed at 100° C. into the tribromide and free bromine. Its reactions resemble those of the corresponding chloride.

Diphosphorous tetriodide, $'P''_2I_4$ (*molecular volume* □□), is prepared by dissolving 5 parts of phosphorus in carbonic disulphide, and gradually adding 41 parts of iodine, cooling well with water during the operation. On concentrating the solution by distilling off the carbonic disulphide, diphosphorous tetriodide crystallizes out in orange-colored prisms fusing at 110° C. (230° F.). Water decomposes it with formation of hydriodic and phosphorous acids and liberation of phosphorus in the amorphous condition:

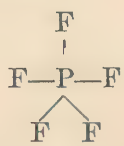
$$\underset{\text{Diphosphorous tetriodide.}}{3'P''_2I_4} + \underset{\text{Water.}}{12OH_2} = \underset{\text{Hydriodic acid.}}{12HI} + \underset{\text{Phosphorous acid.}}{4PHo_3} + P_2.$$

Phosphorous iodide, PI_3, is obtained in the same manner as the foregoing compound, but employing 12 parts of iodine to 1 of phosphorus. It forms dark-red, deliquescent crystals, fusing at 55° C. (131° F.). It cannot be distilled without decomposition. By the action of water it yields hydriodic and phosphorous acids:

$$\underset{\text{Phosphorous iodide.}}{PI_3} + \underset{\text{Water.}}{3OH_2} = \underset{\text{Hydriodic acid.}}{3HI} + \underset{\text{Phosphorous acid.}}{PHo_3}.$$

PHOSPHORIC FLUORIDE.

PF_5.



Molecular weight = 126. *Molecular volume* □□. 1 *litre of phosphoric fluoride weighs* 63 *criths.*

Preparation.—This compound is formed when arsenious fluoride is added to phosphoric chloride:

$$\underset{\text{Arsenious fluoride.}}{5AsF_3} + \underset{\text{Phosphoric chloride.}}{3PCl_5} = \underset{\text{Arsenious chloride.}}{5AsCl_3} + \underset{\text{Phosphoric fluoride.}}{3PF_5}.$$

Properties.—Phosphoric fluoride is a colorless gas which fumes in contact with moist air, and possesses a very irritating odor. It is not inflammable. It is not decomposed by a series of electric sparks, either when the pure gas is employed, or when it is mixed with oxygen or hydrogen.

Reactions.—1. Water decomposes it, forming phosphoric and hydrofluoric acids:

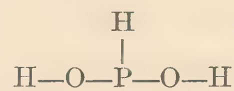
$$\underset{\text{Phosphoric fluoride.}}{\mathbf{PF_5}} + \underset{\text{Water.}}{\mathbf{4OH_2}} = \underset{\text{Phosphoric acid.}}{\mathbf{POHo_3}} + \underset{\text{Hydrofluoric acid.}}{\mathbf{5HF}}.$$

2. It unites with dry ammonia, forming a white solid compound of the formula $2\mathbf{PF}_5,5\mathbf{NH}_3$.

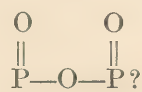
Phosphoric fluoride is particularly interesting as an example of the union of pentadic phosphorus with five monad atoms to form a compound capable of existing in the gaseous state, and even of sustaining very high temperatures without dissociation.

COMPOUNDS OF PHOSPHORUS WITH OXYGEN AND HYDROXYL.

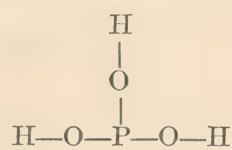
Hypophosphorous acid, . . $\mathbf{PHHo_2}$.



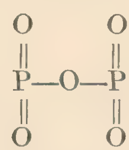
Phosphorous anhydride, . . $\mathbf{P_2O_3}$?



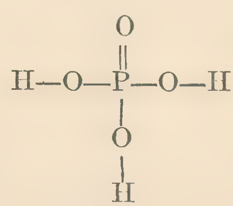
Phosphorous acid, ... $\mathbf{PHo_3}$.



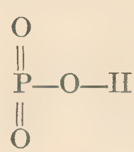
Phosphoric anhydride, . . $\mathbf{P_2O_5}$.



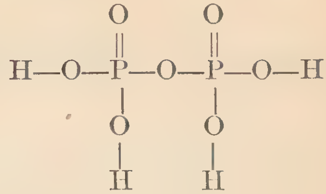
Phosphoric acid (tribasic), . $\mathbf{POHo_3}$.



Metaphosphoric acid (monobasic), ... $\mathbf{PO_2Ho}$.

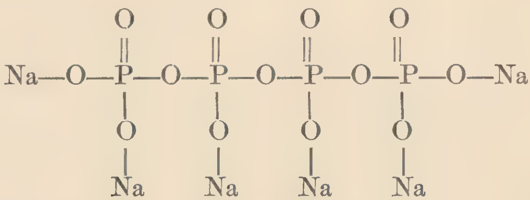


Pyrophosphoric acid (tetrabasic), ... $\mathbf{P}_2O_3Ho_4$.



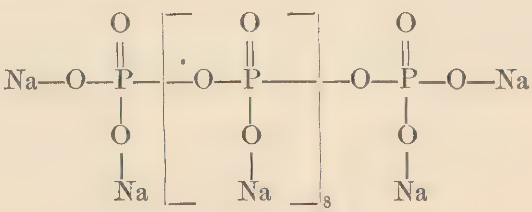
Hexabasic phosphoric acid, . $\mathbf{P}_4O_7Ho_6$.

Sodium salt (Fleitmann and Henneberg) (*Hexasodic tetraphosphate*), ... $\mathbf{P}_4O_7Nao_6$.

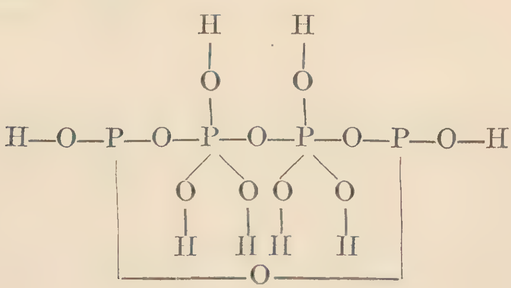


Dodecabasic phosphoric acid, $\mathbf{P}_{10}O_{19}Ho_{12}$.

Sodium salt (Fleitmann and Henneberg) (*Dodecasodic decaphosphate*) . $\mathbf{P}_{10}O_{19}Nao_{12}$.



Phosphorosophosphoric acid (*Hypophosphoric acid*), . $\mathbf{P}_4O_4Ho_8$.



HYPOPHOSPHOROUS ACID.

$PHHo_2$.

Molecular weight = 66. *Fuses at* 17.4° C. (63.3° F.).

Preparation.—When phosphorus is heated with a solution of baric hydrate, phosphoretted hydrogen is evolved and baric hypophosphite is formed:

$$\underset{\text{Baric hydrate.}}{3BaHo_2} + 2P_4 + \underset{\text{Water.}}{6OH_2} = \underset{\text{Baric hypophosphite.}}{3\begin{matrix}PHHo\\PHHo\end{matrix}Bao''} + \underset{\text{Phosphoretted hydrogen.}}{2PH_3}.$$

Any phosphoric acid which is formed at the same time combines with the barium to form insoluble baric phosphate, which may be removed by filtration. To the solution of baric hypophosphite a quantity of dilute sulphuric acid exactly sufficient to precipitate the barium is added, and in this way a solution of hypophosphorous acid is obtained. The clear solution is evaporated over a flame, without, however, allowing it to boil, until the temperature rises to 130° C. (266° F.). On cooling to 0° C. the liquid thus obtained, hypophosphorous acid is deposited in crystals.

Properties.—Hypophosphorous acid forms white laminæ fusing at 17.4° C. (63.3° F.).

Reactions.—1. When strongly heated, hypophosphorous acid is decomposed into phosphoric acid and phosphoretted hydrogen:

$$\underset{\text{Hypophosphorous acid.}}{2PHHo_2} = \underset{\text{Phosphoric acid.}}{POHo_3} + \underset{\text{Phosphoretted hydrogen.}}{PH_3}.$$

2. It readily absorbs oxygen from the air, and is ultimately converted into phosphoric acid:

$$\underset{\text{Hypophosphorous acid.}}{PHHo_2} + O_2 = \underset{\text{Phosphoric acid.}}{POHo_3}.$$

Its affinity for oxygen causes it to act as a powerful reducing agent. It precipitates many of the metals in the metallic state from the solutions of their salts and, when heated with sulphuric acid, reduces it to sulphurous acid, and even to sulphur.

Hypophosphites.—Hypophosphorous acid is a very weak acid, and although it contains two semi-molecules of hydroxyl, its acid power is exhausted as soon as the hydrogen of one of these is replaced by a metal. It therefore acts as a monobasic acid (cf. *Orthophosphates*). The hypophosphites are all soluble in water, and some are crystallizable. They exhibit the same reducing properties as the free acid, and undergo a similar decomposition on heating.

PHOSPHOROUS ANHYDRIDE.

P_2O_3 (?).

Molecular weight = 110 (?).

Preparation.—When phosphorus is gently heated in a slow current of dry air, it burns with a greenish flame, forming a compound having the composition of an anhydride of phosphorous acid.

Properties.—This compound is a white amorphous fusible powder which may be sublimed. It has an odor of garlic.

Reactions.—By allowing the above compound to deliquesce, with exclusion of oxygen, carefully avoiding any rise of temperature, a yellow solution is obtained which has a neutral reaction, and may, by dialysis, be proved to contain a colloid. If the solution be now heated, a reddish substance of unknown composition separates, and the solution contains phosphorous acid, PHo_3. When the so-called anhydride is dissolved in water in the ordinary way, the temperature rises so high as to bring about the above decomposition at once, and a solution of phosphorous acid is obtained with separation of the reddish substance.

From the above, it is probable that the compound obtained when phosphorus is burnt in a limited supply of air is not the true anhydride of phosphorous acid, but a compound of the same composition with a higher molecular weight (compare the molecular weights of arsenious anhydride and antimonious anhydride). The hydrate which this compound forms is neutral, and is therefore not phosphorous acid. The colloidal condition of this hydrate also points to a higher molecular weight. Phosphorous acid is formed only when this hydrate is decomposed by heating (Reinitzer).

PHOSPHOROUS ACID.

PHo_3.

Molecular weight = 82. *Fuses at* 70° C. (158° F.).

Preparation.—1. Phosphorous acid is formed by the action of water upon the so-called phosphorous anhydride as above described.

2. It may also be obtained by the spontaneous oxidation of phosphorus in moist air. In this process, however, a portion of the phosphorous acid always undergoes further oxidation to phosphoric acid. Phosphorosophosphoric acid (*q.v.*) is also formed.

3. It is best obtained in a state of purity by the action of water on phosphorous chloride (see p. 345). It is not necessary to prepare the phosphorous chloride separately. Phosphorus is melted under water, and a stream of chlorine is passed through the phosphorus, the phosphorous chloride being thus decomposed by the water as fast as it is formed. The reaction must be interrupted before all the phosphorus has disap-

peared, otherwise the excess of the chlorine in presence of water will oxidize the phosphorous acid to phosphoric acid. The solution of hydrochloric and phosphorous acids is evaporated, gradually raising the temperature to 180°, by which means the last traces of water are expelled.

Properties.—Phosphorous acid is a white, crystalline, very soluble mass, fusing at 70° C. (158° F.).

Reactions.—1. When heated above 180° C. (356° F.), it yields phosphoric acid and phosphoretted hydrogen:

$$\underset{\text{Phosphorous acid.}}{4\mathbf{P}\mathrm{Ho}_3} = \underset{\text{Phosphoric acid.}}{3\mathbf{PO}\mathrm{Ho}_3} + \underset{\text{Phosphoretted hydrogen.}}{\mathbf{P}\mathrm{H}_3}.$$

2. When treated with oxidizing agents, or when exposed to the air, it yields phosphoric acid:

$$\underset{\text{Phosphorous acid.}}{2\mathbf{P}\mathrm{Ho}_3} + \mathrm{O}_2 = \underset{\text{Phosphoric acid.}}{2\mathbf{PO}\mathrm{Ho}_3}.$$

Owing to its affinity for oxygen it acts as a powerful reducing agent. Solutions of silver salts, when warmed with it, deposit metallic silver; mercuric chloride is reduced to mercurous chloride; and cupric sulphate yields a precipitate of cuprous hydride.

Phosphites.—Phosphorous acid is a tribasic acid; but only the monobasic and dibasic salts are stable. The normal sodium salt, $\mathbf{P}\mathrm{Nao}_3$, is obtained by dissolving phosphorous acid in an excess of sodic hydrate and adding absolute alcohol to the solution, when the salt is precipitated as an uncrystallizable syrup. It is decomposed by water (Zimmermann).

The phosphites are decomposed on heating, with evolution of phosphoretted hydrogen and formation of metaphosphates and pyrophosphates. The soluble salts have a reducing action.

PHOSPHORIC ANHYDRIDE.

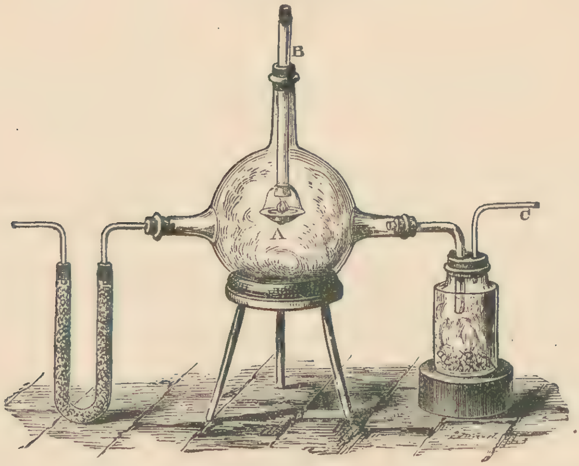
$\mathbf{P}_2\mathrm{O}_5$.

Molecular weight = 142.

Preparation.—Phosphoric anhydride is obtained by burning phosphorus in an excess of dry air or oxygen. A stream of air, dried by passing through a U-tube containing pumice moistened with sulphuric acid, is drawn by means of an aspirator, attached to the tube C, through the three-necked globe (Fig. 47). Thoroughly dried phosphorus is introduced through the tube B into the capsule A, and is then lighted by touching it with a hot wire, the tube being then closed with a cork. As soon as one piece of phosphorus is consumed, a fresh piece is introduced in the same way, and is now at once ignited by the hot capsule.

The phosphoric anhydride collects in the globe, whilst any particles which are carried off by the current of air are retained in the bottle.

FIG. 47.



Properties.—Phosphoric anhydride is a white, voluminous, amorphous powder, which may be sublimed at a high temperature.

Reaction.—When brought in contact with water it hisses violently, evolving great heat and dissolving with formation of metaphosphoric acid:

$$\underset{\text{Phosphoric anhydride.}}{P_2O_5} + \underset{\text{Water.}}{OH_2} = \underset{\text{Metaphosphoric acid.}}{2PO_2Ho.}$$

When exposed to the air it rapidly absorbs moisture and deliquesces. It is the most powerful desiccating agent known, and is employed in the laboratory for removing moisture from gases and liquids. Many substances containing oxygen and hydrogen are decomposed by it, as it abstracts these elements in the proportions necessary to form water.

METAPHOSPHORIC ACID.

$PO_2Ho.$

Molecular weight = 80.

Preparation.—1. Metaphosphoric acid is formed by dissolving phosphoric anhydride in cold water (see above).

2. It may be obtained by heating tribasic phosphoric acid to redness:

$$\underset{\text{Orthophosphoric acid.}}{POHo_3} = \underset{\text{Metaphosphoric acid.}}{PO_2Ho} + \underset{\text{Water.}}{OH_2.}$$

Properties.—Metaphosphoric acid forms a transparent vitreous mass which is readily soluble in water. It is fusible, and at a high temperature may be volatilized. Its solutions coagulate albumen.

Reaction.—In aqueous solution, metaphosphoric acid is gradually converted into tribasic phosphoric acid:

$$\underset{\text{Metaphosphoric acid.}}{PO_2Ho} + \underset{\text{Water.}}{OH_2} = \underset{\text{Orthophosphoric acid.}}{POHo_3}.$$

This change takes place rapidly on boiling.

Metaphosphates.—These salts may be obtained:

1. By igniting the dihydric phosphate of a fixed base:

$$\underset{\text{Dihydric sodic phosphate.}}{POHo_2Nao} = \underset{\text{Sodic metaphosphate.}}{PO_2Nao} + \underset{\text{Water.}}{OH_2}.$$

2. By igniting a monohydric phosphate which contains one atom of a volatile base:

$$\underset{\text{Hydric sodic ammonic phosphate.}}{POHoNao(N^vH_4O)} = \underset{\text{Sodic metaphosphate.}}{PO_2Nao} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{OH_2}.$$

3. By igniting a dihydric pyrophosphate:

$$\underset{\text{Dihydric disodic pyrophosphate.}}{P_2O_3Ho_2Nao_2} = \underset{\text{Sodic metaphosphate.}}{2PO_2Nao} + \underset{\text{Water.}}{OH_2}.$$

Properties of the Metaphosphates.—The metaphosphates are remarkable as existing in several distinct modifications, referable to different polymeric varieties of metaphosphoric acid. Most of these acids form double salts, and from the relative number of atoms of the two bases contained in such a salt, the minimum molecular weight of the acid may be determined. Thus, *hexametaphosphoric acid,* $P_6O_{12}Ho_6$, forms a double salt of the formula

$$\begin{matrix} P_6O_{12}NaoCao''_2 \\ P_6O_{12}NaoCao''_2 \end{matrix} Cao''.$$

The soluble metaphosphates are converted into dihydric tribasic phosphates by continued boiling with water; the insoluble metaphosphates are converted in a similar manner by boiling with dilute nitric acid. The soluble metaphosphates yield with argentic nitrate a gelatinous white precipitate of argentic metaphosphate.

PYROPHOSPHORIC ACID.

$$P_2O_3Ho_4.$$

Molecular weight = 178.

Preparation.—1. Pyrophosphoric acid is prepared by heating tribasic phosphoric acid for some time to 213° C.:

$2POHo_3$	=	$P_2O_3Ho_4$	+	OH_2.
Phosphoric acid.		Pyrophosphoric acid.		Water.

2. An aqueous solution of this acid is obtained by suspending plumbic pyrophosphate (prepared by precipitating sodic pyrophosphate with a soluble lead salt) in water, and decomposing it with sulphuretted hydrogen:

$P_2O_3Pbo''_2$	+	$2SH_2$	=	$2PbS''$	+	$P_2O_3Ho_4$.
Plumbic pyrophosphate.		Sulphuretted hydrogen.		Plumbic sulphide.		Pyrophosphoric acid.

Properties.—Pyrophosphoric acid forms a colorless opaque crystalline mass. It is readily soluble in water. The solution does not coagulate albumen.

Reactions.—1. In solution, pyrophosphoric acid is converted slowly at ordinary temperatures, rapidly on boiling, into tribasic phosphoric acid:

$P_2O_3Ho_4$	+	OH_2	=	$2POHo_3$.
Pyrophosphoric acid.		Water.		Orthophosphoric acid.

2. On heating to redness it yields metaphosphoric acid:

$P_2O_3Ho_4$	=	$2PO_2Ho$	+	OH_2.
Pyrophosphoric acid.		Metaphosphoric acid.		Water.

Pyrophosphates.—These salts are prepared by heating tribasic phosphates in which two atoms of the hydrogen of the acid are replaced by a fixed base:

$2POHoNao_2$	=	$P_2O_3Nao_4$	+	OH_2.
Hydric disodic phosphate.		Sodic pyrophosphate.		Water.

$2POMgo''(NH_4O)$	=	$P_2O_3Mgo''_2$	+	$2NH_3$	+	OH_2.
Magnesic ammonic phosphate.		Magnesic pyrophosphate.		Ammonia.		Water.

Pyrophosphoric acid is a tetrabasic acid and forms four classes of salts. Only the alkaline pyrophosphates are soluble in water; but the other pyrophosphates are soluble in acids, and generally also

in an excess of an alkaline pyrophosphate, forming, in the latter case, soluble double salts. With argentic nitrate the alkaline pyrophosphates yield a white granular precipitate of argentic pyrophosphate; with soluble salts of copper, a double salt, of the formula $\begin{matrix} P_2O_3NaoCuo'' \\ P_2O_3NaoCuo'' \end{matrix}Cuo''$, is obtained. The solutions of the pyrophosphates are perfectly stable, even when boiled. By boiling with dilute acids, however, the pyrophosphates are converted into tribasic phosphates.

PHOSPHORIC ACID, *Tribasic Phosphoric Acid, Orthophosphoric Acid.*

$$POHo_3.$$

Molecular weight = 98. *Fuses at* 38.6° C. (101.5° F.).

Preparation.—1. This acid is formed when phosphoric anhydride, metaphosphoric acid, or pyrophosphoric acid is boiled with water for some time:

$$\underset{\text{Phosphoric anhydride.}}{P_2O_5} + \underset{\text{Water.}}{3OH_2} = \underset{\text{Orthophosphoric acid.}}{2POHo_3.}$$

2. It is best prepared in a state of purity by heating amorphous phosphorus with concentrated nitric acid. The oxidation is complete when red fumes cease to be evolved on the addition of fresh nitric acid. The excess of nitric acid is then driven off by evaporation.

3. It is formed by the action of water upon phosphoric chloride (p. 346) and phosphoric oxytrichloride (*q.v.*).

4. It is prepared on a large scale by treating 3 parts of bone-ash or phosphorite with 2 parts of sulphuric acid and 10 parts of water, heating the mixture for some days:

$$\underset{\text{Tricalcic phosphate.}}{P_2O_2Cao''_3} + \underset{\text{Sulphuric acid.}}{3SO_2Ho_2} + \underset{\text{Water.}}{6OH_2} = \underset{\text{Phosphoric acid.}}{2POHo_3} + \underset{\text{Gypsum (Tetrahydric calcic sulphate).}}{3SHo_4Cao''.}$$

The solution is filtered from the insoluble calcic sulphate.

The phosphoric acid prepared by any of the above methods, must be heated to 150° C. (302° F.) to expel the last traces of water.

Properties.—Phosphoric acid forms transparent prisms, fusing at 38.6° C. (101.5° F.). When exposed to the air, it deliquesces to a syrupy liquid. Its solution does not coagulate albumen.

Phosphates.—Phosphoric acid is a tribasic acid, forming three classes of salts, of which the following are examples:

Trisodic phosphate, ...	$PONao_3,2OH_2$.
Hydric disodic phosphate, . . .	$POHoNao_2,12OH_2$.
Dihydric sodic phosphate, . . .	$POHo_2Nao,OH_2$.

The *normal salts*, with the exception of those of the alkalies, are insoluble in water. Trilithic phosphate ($POLio_3$) is only sparingly soluble. The solutions of the normal alkaline phosphates have an alkaline reaction. In solution they are decomposed by carbonic anhydride with formation of monohydric phosphates:

$PONao_3$	+	CO_2	+	OH_2	=	$POHoNao_2$	+	$COHoNao$.
Trisodic phosphate.		Carbonic anhydride.		Water.		Hydric disodic phosphate.		Hydric sodic carbonate.

Dilute acids produce this change in the insoluble normal phosphates, dissolving them with formation of monohydric phosphates.

The *monohydric phosphates* of the alkalies are soluble in water, and have a feebly alkaline reaction.

The *dihydric phosphates* have an acid reaction. These compounds are sometimes referred to as *superphosphates*.

The heavy metals form, as a rule, only normal phosphates, the other phosphates existing only in solution in presence of an excess of acid. If argentic nitrate be added to a solution of any of the alkaline phosphates, a yellow precipitate of triargentic phosphate is formed:

$PONao_3$	+	$3NO_2Ago$	=	$POAgo_3$	+	$3NO_2Nao$.
Trisodic phosphate.		Argentic nitrate.		Triargentic phosphate.		Sodic nitrate.

$POHoNao_2$	+	$3NO_2Ago$	=	$POAgo_3$	+	$2NO_2Nao$	+	NO_2Ho.
Hydric disodic phosphate.		Argentic nitrate.		Triargentic phosphate.		Sodic nitrate.		Nitric acid.

$POHo_2Nao$	+	$3NO_2Ago$	=	$POAgo_3$	+	NO_2Nao	+	$2NO_2Ho$.
Dihydric sodic phosphate.		Argentic nitrate.		Triargentic phosphate.		Sodic nitrate.		Nitric acid.

It is worthy of note that, in the second of these reactions, by the mixture of two solutions, one of which is neutral and the other slightly alkaline, an acid liquid is produced.

The soluble phosphates also yield a white crystalline precipitate of ammonic magnesic phosphate, $PO(N^vH_4O)Mgo'',6OH_2$, when a clear solution of magnesic sulphate and ammonic chloride containing an excess of ammonia is added to their solutions; this precipitate is insoluble in water containing free ammonia, and on ignition is converted into magnesic pyrophosphate, $P_2O_3Mgo''_2$. With a solution of ammonic molybdate in nitric acid, they yield, especially on warming, a yellow precipitate of ammonic phosphomolybdate (*q.v.*).

The following are some of the more important naturally occurring phosphates:

Apatite (*Francolite*)	$P_3O_3Cao''_4\left(\begin{matrix}O\\F\end{matrix}Ca''\right)$.*
Vivianite, ...	$P_2O_2Feo''_3,8OH_2$.
Wavellite, ...	$P_4O('Al'''_2O_6)^{vi}_3,12OH_2$.
Pyromorphite, ...	$P_3O_3Pbo''_4\left(\begin{matrix}O\\Cl\end{matrix}Pb''\right)$.

* In this mineral, chlorine and fluorine displace each other isomorphously.

Some of the acids of phosphorus have a tendency to exhibit a basicity lower than their hydricity. Thus, though phosphoric acid forms tribasic salts, the last equivalent of base is so loosely attached, that in the case of the soluble tribasic phosphates, it is removed by carbonic anhydride. In the case of phosphorous acid, a weaker acid, the tribasic salts are decomposed even by water, whilst hypophosphorous acid, a still weaker acid, forms only salts with one equivalent of base, though its formula would show it to be dibasic.

PHOSPHOROSOPHOSPHORIC ACID (*Hypophosphoric Acid*).

$$P_4O_4Ho_8.$$

Molecular weight = 324.

Preparation.—When phosphorus is allowed to oxidize spontaneously by exposure to air and in contact with water, an acid liquid is obtained, which contains phosphorous acid, phosphoric acid, and phosphorosophosphoric acid. As the latter acid, when in solution, gradually undergoes decomposition, the liquid is to be removed at the end of about three days. On adding sodic acetate a crystalline precipitate of *tetrahydric tetrasodic phosphorosophosphate*, $P_4O_4Ho_4Nao_4,12OH_2$, is formed, which by recrystallization may be obtained in tabular crystals. The free acid is prepared by precipitating the barium salt with sulphuric acid or the lead salt with sulphuretted hydrogen.

Reactions.—Phosphorosophosphoric acid can be obtained only in solution. On evaporation over sulphuric acid, or even on standing at ordinary temperatures, it undergoes decomposition into phosphorous and pyrophosphoric acids:

$$\underset{\text{Phosphoroso-phosphoric acid.}}{P_4O_4Ho_8} + \underset{\text{Water.}}{OH_2} = \underset{\text{Pyrophosphoric acid.}}{P_2O_3Ho_4} + \underset{\text{Phosphorous acid.}}{2PHo_3}.$$

Phosphorosophosphates.—These salts crystallize well. Owing to the high basicity of the acid, they are generally complex. The phosphorophosphates of potassium will serve as examples:

Potassic phosphorosophosphate, ...	$P_4O_4Ko_8,16OH_2$
Dihydric hexapotassic phosphorosophosphate,	$P_4O_4Ho_2Ko_6,6OH_2$.
Tetrahydric tetrapotassic phosphorosophosphate,	$P_4O_4Ho_4Ko_4,4OH_2$, also $6OH_2$.
Pentahydric tripotassic phosphorosophosphate,	$P_4O_4Ho_5Ko_3,2OH_2$.
Hexahydric dipotassic phosphorosophosphate,	$P_4O_4Ho_6Ko_2$.

That phosphorosophosphoric acid has at least the molecular weight here ascribed to it is rendered probable by the existence of such a salt as pentahydric tripotassic phosphorosophosphate, and by the above decomposition of the free acid into a mixture of phosphorous and pyrophosphoric acids.

COMPOUNDS OF PHOSPHORUS WITH CHLORINE AND OXYGEN.

PHOSPHORIC OXYTRICHLORIDE, *Phosphorylic Chloride.*

$$POCl_3. \qquad \begin{array}{c} Cl \\ | \\ Cl{-}P{-}Cl \\ \| \\ O \end{array}$$

Molecular weight = 153.5. *Molecular volume* $\square\!\square$. 1 *litre of phosphoric oxytrichloride vapor weighs* 76.75 *criths. Sp. gr.* 1.7. *Fuses at* —1.5° C. (29.3° F.). *Boils at* 110° C. (230° F.).

Preparation.—1. Phosphoric oxytrichloride may be prepared by decomposing phosphoric chloride with a limited quantity of water:

PCl_5	+	OH_2	=	$POCl_3$	+	$2HCl.$
Phosphoric chloride.		Water.		Phosphoric oxytrichloride.		Hydrochloric acid.

2. It is formed when oxygen is passed through boiling phosphorous chloride:

PCl_3	+	O	=	$POCl_3.$
Phosphorous chloride.				Phosphoric oxytrichloride.

3. It may be readily obtained by heating together in a sealed tube a mixture of phosphoric chloride and phosphoric anhydride:

P_2O_5	+	$3PCl_5$	=	$5POCl_3.$
Phosphoric anhydride.		Phosphoric chloride.		Phosphoric oxychloride.

4. It is formed by the action of phosphoric chloride on various organic and inorganic compounds containing oxygen (p. 346), and is best prepared by heating dried oxalic acid or boric acid with phosphoric chloride:

$\left\{\begin{array}{l}COHo\\COHo\end{array}\right.$	+	PCl_5	=	$POCl_3$	+	CO_2	+	CO	+	$2HCl.$
Oxalic acid.		Phosphoric chloride.		Phosphoric oxytrichloride.		Carbonic anhydride.		Carbonic oxide.		Hydrochloric acid.

$2BHo_3$	+	$3PCl_5$	=	$3POCl_3$	+	B_2O_3	+	$6HCl.$
Boric acid.		Phosphoric chloride.		Phosphoric oxytrichloride.		Boric anhydride.		Hydrochloric acid.

Properties.—Phosphoric oxytrichloride is a colorless powerfully refracting liquid which fumes in contact with moist air. In a freezing

mixture it solidifies at —10° C. (14° F.) to a laminar crystalline mass fusing at —1.5° C. (29.3° F.).

Reactions.—1. By contact with water it is slowly transformed into hydrochloric and phosphoric acids:

$$\underset{\text{Phosphoric oxytrichloride.}}{POCl_3} + \underset{\text{Water.}}{3OH_2} = \underset{\text{Phosphoric acid.}}{POHo_3} + \underset{\text{Hydrochloric acid.}}{3HCl.}$$

2. By distillation with the salts of acids, it yields the corresponding acid chlorides:

$$\underset{\text{Plumbic sulphate.}}{3SO_2Pbo''} + \underset{\text{Phosphoric oxytrichloride.}}{2POCl_3} = \underset{\text{Plumbic phosphate.}}{{}^{PO}_{PO}Pbo''_3} + \underset{\text{Sulphuric oxydichloride.}}{3SO_2Cl_2.}$$

$$\underset{\text{Sodic acetate.}}{3\left\{\begin{matrix}CH_3\\ CONao\end{matrix}\right.} + \underset{\text{Phosphoric oxytrichloride.}}{POCl_3} = \underset{\text{Acetylic chloride.}}{3\left\{\begin{matrix}CH_3\\ COCl\end{matrix}\right.} + \underset{\text{Sodic phosphate.}}{PONao_3.}$$

Phosphoric oxytrichloride is itself the acid chloride of phosphoric acid. This relation, which is better expressed by the name *Phosphorylic chloride,* is displayed in the above decomposition of this substance with water.

The corresponding bromine compound $POBr_3$ (*molecular volume* $\boxed{}\boxed{}$) is obtained in a similar manner by the action of a limited quantity of water on phosphoric bromide. It forms a crystalline mass fusing at 45–46° C. (113–115° F.), and boiling at 195° C. (383° F.).

PYROPHOSPHORYLIC CHLORIDE.

$$P_2O_3Cl_4. \qquad \begin{array}{ccccccccc} & & O & & & & O & & \\ & & \| & & & & \| & & \\ Cl & — & P & — & O & — & P & — & Cl \\ & & | & & & & | & & \\ & & Cl & & & & Cl & & \end{array}$$

Molecular weight = 252. *Sp. gr.* 1.58 *at* 7° C. *Boils with partial decomposition at* 210–215° C.

Preparation.—This compound is prepared by passing gaseous nitric peroxide into phosphorous chloride, and distilling the liquid thus obtained. The portion which passes over between 200° and 230° C. is pyrophosphorylic chloride. This product must be purified by rectification. The reaction is a very complicated one, and cannot be expressed by a single equation. The by-products are phosphoric oxytrichloride, phosphoric anhydride, nitrous oxychloride, and nitrogen.

Properties.—Pyrophosphorylic chloride is a colorless fuming liquid.

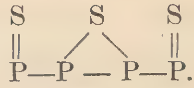
Reactions.—1. Water decomposes it instantaneously with formation of orthophosphoric (not pyrophosphoric) and hydrochloric acids:

$$\underset{\text{Pyrophosphorylic chloride.}}{P_2O_3Cl_4} + \underset{\text{Water.}}{5OH_2} = \underset{\text{Orthophosphoric acid.}}{2POHo_3} + \underset{\text{Hydrochloric acid.}}{4HCl.}$$

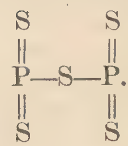
2. When treated with phosphoric chloride, phosphoric oxytrichloride is formed:

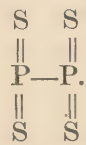
$$\underset{\text{Pyrophosphorylic chloride.}}{P_2O_3Cl_4} + \underset{\text{Phosphoric chloride.}}{PCl_5} = \underset{\text{Phosphoric oxytrichloride.}}{3POCl_3.}$$

COMPOUNDS OF PHOSPHORUS WITH SULPHUR.

Tetraphosphorus trisulphide, . $^{vi}(\mathbf{P}_4)^{vi}S''_3$. 

Phosphorous sulphide, . . . $\mathbf{P}_2S''_3$. 

Phosphoric sulphide, . . . $\mathbf{P}_2S''_5$. 

Diphosphoric tetrasulphide, . $'\mathbf{P}^{iv}{}_2S''_4$. 

These compounds are all formed by the direct union of their elements. Amorphous phosphorus and sulphur are heated together in the proportions required by the formulæ. With ordinary phosphorus, the combination is apt to take place with explosive violence.

TETRAPHOSPHORUS TRISULPHIDE.

$^{vi}(\mathbf{P}_4)^{vi}S''_3$.

Molecular weight = 220. *Molecular volume* $\square\square$. 1 *litre of the vapor weighs* 110 *criths. Fuses at* 166° C. (330.8° F.). *Boils between* 300° *and* 400° C.

Preparation.—A mixture of amorphous phosphorus and sulphur in the proportions expressed by the formula P_4S_3 is heated for eight hours to a temperature of 260° C. (500° F.). The substance is thus obtained as a yellow translucent mass, which is purified by crystallization from carbonic disulphide.

Properties.—It forms yellowish prisms with a pyramidal termination.

Reaction.—Boiling with water slowly decomposes it, with formation of phosphorous acid, phosphoretted hydrogen, and sulphuretted hydrogen:

$^{vi}(\mathbf{P}_4)^{vi}S''_3$	+	$9\mathbf{O}H_2$	=	$3\mathbf{P}HO_3$	+	$\mathbf{P}H_3$	+	$3\mathbf{S}H_2$.
Tetraphosphorus sulphide.		Water.		Phosphorous acid.		Phosphoretted hydrogen.		Sulphuretted hydrogen.

PHOSPHOROUS SULPHIDE.

$\mathbf{P}_2S''_3$.

Molecular weight = 158.

Preparation.—As above.

Properties.—Phosphorous sulphide forms a greyish-yellow crystalline mass melting at about 290° C. (554° F.). It has not been obtained in definite crystals, and has not been distilled.

Reaction.—Water decomposes it, forming phosphorous acid and sulphuretted hydrogen:

$\mathbf{P}_2S''_3$	+	$6\mathbf{O}H_2$	=	$2\mathbf{P}HO_3$	+	$3\mathbf{S}H_2$.
Phosphorous sulphide.		Water.		Phosphorous acid.		Sulphuretted hydrogen.

PHOSPHORIC SULPHIDE.

$$P_2S''_5.$$

Molecular weight = 222. *Molecular volume* $\square\square$. 1 *litre of the vapor weighs* 111 *criths. Fuses at* 274–276° C. (525–529° F.). *Boils at* 530° C. (986° F.).

Preparation.—As above. The process may also be modified by dissolving ordinary phosphorus and sulphur in the molecular proportions, $P_2S''_5$, in carbonic disulphide, and heating the solution in sealed tubes for 8–10 hours to 210° C. (410° F.). On cooling, the phosphoric sulphide is deposited on the walls of the tube in well-formed crystals.

Properties.—It forms pale-yellow crystals generally grouped in tufts.

Reactions.—1. By direct combination with alkaline sulphides it forms the sulphophosphates:

$$\underset{\text{Phosphoric sulphide.}}{P_2S''_5} + \underset{\text{Potassic sulphide.}}{3SK_2} = \underset{\text{Potassic sulphophosphate.}}{2PS''Ks_3.}$$

2. With water phosphoric sulphide yields phosphoric acid and sulphuretted hydrogen:

$$\underset{\text{Phosphoric sulphide.}}{P_2S''_5} + \underset{\text{Water.}}{8OH_2} = \underset{\text{Phosphoric acid.}}{2POHo_3} + \underset{\text{Sulphuretted hydrogen.}}{5SH_2.}$$

Phosphoric sulphide is employed in the laboratory for the purpose of replacing oxygen by sulphur in organic compounds.

DIPHOSPHORIC TETRASULPHIDE.

$$'P^{iv}{}_2S''_4.$$

Molecular weight = 190.* *Fuses at* 296–298° C.

Preparation.—Phosphorus and sulphur in the proportions corresponding with the formula P_2S_4 are dissolved in carbonic disulphide and heated in sealed tubes.

Properties.—It is thus obtained in the form of yellow transparent acicular crystals. It boils without decomposition.

COMPOUND OF PHOSPHORUS WITH SULPHUR AND CHLORINE.

PHOSPHORIC SULPHOTRICHLORIDE.

$$PS''Cl_3. \quad \begin{array}{c} Cl \\ | \\ Cl—P—Cl. \\ \| \\ S \end{array}$$

Molecular weight = 169.5. *Molecular volume* $\square\square$. 1 *litre of the vapor weighs* 84.75 *criths. Sp. gr. of liquid* 1.636 *at* 20° C. *Boils at* 126° C. (259° F.).

Preparation.—1. Phosphoric sulphotrichloride is best prepared by heating together phosphoric sulphide and phosphoric chloride for a few minutes to 150° C. (302° F.):

* The vapor-density of this compound has been determined with a result which would point to the formula P_3S_6. This anomalous result is possiby due to the employment of too low a temperature in the determination.

$$\underset{\text{Phosphoric sulphide.}}{P_2S''_5} + \underset{\text{Phosphoric chloride.}}{3PCl_5} = \underset{\text{Phosphoric sulphotrichloride.}}{5PS''Cl_3}.$$

2. It is also formed by the action of sulphuretted hydrogen upon phosphoric chloride:

$$\underset{\text{Phosphoric chloride.}}{PCl_5} + \underset{\text{Sulphuretted hydrogen.}}{SH_2} = \underset{\text{Phosphoric sulphotrichloride.}}{PS''Cl_3} + \underset{\text{Hydrochloric acid.}}{2HCl}.$$

Properties.—It is a colorless fuming liquid.

Reactions.—1. Water slowly decomposes it, yielding hydrochloric acid, phosphoric acid, and sulphuretted hydrogen:

$$\underset{\text{Phosphoric sulphotrichloride.}}{PS''Cl_3} + \underset{\text{Water.}}{4OH_2} = \underset{\text{Phosphoric acid.}}{POHo_3} + \underset{\text{Hydrochloric acid.}}{3HCl} + \underset{\text{Sulphuretted hydrogen.}}{SH_2}.$$

2. With alkalies it yields the salts of sulphophosphoric acid ($PS''Ho_3$):

$$\underset{\text{Phosphoric sulphotrichloride.}}{PS''Cl_3} + \underset{\text{Potassic hydrate.}}{6OKH} = \underset{\text{Potassic sulphophosphate.}}{PS''Ko_3} + \underset{\text{Potassic chloride.}}{3KCl} + \underset{\text{Water.}}{3OH_2}.$$

The corresponding bromine compound $PS''Br_3$ is also known.

PHOSPHORUS COMPOUNDS CONTAINING NITROGEN.

These substances possess considerable theoretical interest as examples of a class of compounds largely represented in organic, but of rarer occurrence in inorganic, chemistry.

Phospham, $PN(NH)''$, is prepared by passing gaseous ammonia over phosphoric chloride as long as the gas is absorbed, and then igniting the product in a current of carbonic anhydride or some other indifferent gas:

$$\underset{\text{Phosphoric chloride.}}{PCl_5} + \underset{\text{Ammonia.}}{7NH_3} = \underset{\text{Phospham.}}{PN(NH)''} + \underset{\text{Ammonic chloride.}}{5NH_4Cl}.$$

Phospham is a white powder, insoluble in water.

Phosphamimide, $PO(NH)''(NH_2)$, remains behind as a white powder when the product of the action of gaseous ammonia on phosphoric pentachloride is extracted with water:

$$\underset{\text{Phosphoric chloride.}}{PCl_5} + \underset{\text{Ammonia.}}{7NH_3} + \underset{\text{Water.}}{OH_2} = \underset{\text{Phosphamimide.}}{PO(NH)''(NH_2)} + \underset{\text{Ammonic chloride.}}{5NH_4Cl}.$$

Phosphoric oxytriamide, $PO(NH_2)_3$, is obtained as a white amorphous powder by the action of gaseous ammonia on phosphoric oxytrichloride:

$$\underset{\text{Phosphoric oxytrichloride.}}{POCl_3} + \underset{\text{Ammonia.}}{6NH_3} = \underset{\text{Phosphoric oxytriamide.}}{PO(NH_2)_3} + \underset{\text{Ammonic chloride.}}{3NH_4Cl}.$$

The product is well washed with water to remove the ammonic chloride. When this, or the foregoing compound, is ignited in an atmosphere free from oxygen, ammonia is given off, and *phosphoric oxynitride*, PON, remains as a white powder.

Pyrophosphotriamic acid, $P_2O_3(NH_2)_3Ho$, is prepared by saturating phosphoric oxytrichloride with gaseous ammonia without cooling, heating the product to 220° C., and finally boiling it for a short time with water:

$$\underset{\text{Phosphoric oxytrichloride.}}{2POCl_3} + \underset{\text{Ammonia.}}{9NH_3} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Pyrophosphotriamic acid.}}{P_2O_3(NH_2)_3Ho} + \underset{\text{Ammonic chloride.}}{6NH_4Cl}.$$

It forms an amorphous insoluble powder, which is successively converted by continuous boiling with water into soluble *pyrophosphodiamic acid*, $P_2O_3(NH_2)_2Ho_2$, and *pyrophosphamic acid*, $P_2O_3(NH_2)Ho_3$, this last compound being finally transformed into a mixture of ammonic phosphate and phosphoric acid.

VANADIUM, V_4?

Atomic weight = 51.3. *Probable molecular weight* = 205.2. *Sp. gr.* 5.5. *Atomicity* ''' *and* ^{v}. *Evidence of atomicity:*

Vanadous chloride, ...	$\mathbf{V}'''Cl_3$.
Vanadic oxytrichloride, ...	$\mathbf{V}^{v}OCl_3$.

History.—This rare element was discovered in 1801, by Del Rio, who obtained it from a Mexican lead-ore. He failed, however, to recognize its true nature, and ultimately regarded it as impure chromium. In 1830 it was rediscovered independently by Sefström. Metallic vanadium was first isolated by Roscoe.

Occurrence.—Vanadium occurs sparingly in various lead and iron ores. The cupric and bismuthous vanadates constitute the rare minerals *volborthite* and *pucherite*. A relatively rich source of vanadium has lately been found in the Bessemer slag of the Creusot iron works, which contains as much as 1.5 per cent. of this element.

Preparation.—Metallic vanadium is obtained by heating vanadous chloride to bright redness in a current of dry hydrogen:

$$\underset{\text{Vanadous chloride.}}{2\mathbf{V}Cl_3} + 3H_2 = V_2 + \underset{\text{Hydrochloric acid.}}{6HCl.}$$

Properties.—As above prepared it forms a silvery, crystalline mass, of sp. gr. 5.5. It does not oxidize, either in dry or in moist air, even at 100° C. When strongly heated in air or oxygen it burns, forming vanadic anhydride, $\mathbf{V}_2O_5$. It does not fuse at a red heat. Hydrochloric acid is without action upon it; concentrated sulphuric acid dissolves it on heating; and nitric acid, even when dilute, attacks it energetically, dissolving it to form a blue solution. Fused with caustic alkalies it yields a vanadate of the base with evolution of hydrogen.

COMPOUNDS OF VANADIUM WITH CHLORINE.

Hypovanadous chloride, ...	$\left\{\begin{array}{l}\mathbf{V}Cl_2\\ \mathbf{V}Cl_2.\end{array}\right.$
Vanadous chloride, ...	$\mathbf{V}Cl_3$.
Hypovanadic chloride, ...	$'\mathbf{V}^{iv}Cl_4$ or $\left\{\begin{array}{l}\mathbf{V}Cl_4.\\ \mathbf{V}Cl_4.\end{array}\right.$

Hypovanadous chloride, $'\mathbf{V}''_2Cl_4$, is obtained in apple-green micaceous plates by passing the vapor of the trichloride mixed with hydrogen through a red-hot tube:

$$\underset{\text{Vanadous chloride.}}{2\mathbf{V}Cl_3} + H_2 = \underset{\text{Hypovanadous chloride.}}{'\mathbf{V}''_2Cl_4} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

It is hygroscopic, and dissolves in water, yielding a violet solution.

Vanadous chloride, $\mathbf{V}Cl_3$, is prepared from hypovanadic chloride, which is decomposed slowly at ordinary temperatures, rapidly at its boiling-point, into vanadous chloride and free chlorine. It forms peach-blossom-colored tabular crystals, is non-volatile, and deliquesces when exposed to the air.

Hypovanadic chloride, $'\mathbf{V}^{iv}Cl_4$ (*molecular volume* $\square\square$), is formed by the action of an excess of chlorine on metallic vanadium. It may also be obtained by repeatedly passing the vapor of the oxytrichloride, mixed with chlorine, over charcoal:

$$\underset{\text{Vanadic oxytrichloride.}}{2\mathbf{V}OCl_3} + C_2 + Cl_2 = \underset{\text{Hypovanadic chloride.}}{2'\mathbf{V}^{iv}Cl_4} + \underset{\text{Carbonic oxide.}}{2\mathbf{C}O.}$$

It is a dark-brown liquid, boiling at 154° C., and having a sp. gr. of 1.8584 at 0° C. Water decomposes and dissolves it, yielding a blue liquid. The molecular formula, VCl_4, as deduced from the vapor-density of this compound, is anomalous. In such a compound, vanadium would be tetradic, in violation of the law regulating the variation of atomicity; otherwise, the presence of a single free bond must be assumed (see note, p. 179).

COMPOUNDS OF VANADIUM WITH OXYGEN AND HYDROXYL.

Hypovanadous oxide,	$'\mathbf{V}''_2O_2$.
Vanadous oxide,	$\mathbf{V}_2O_3$.
Hypovanadic oxide,	$'\mathbf{V}^{iv}{}_2O_4$.
Vanadic anhydride,	$\mathbf{V}_2O_5$.
Metavanadic acid,	$\mathbf{V}O_2Ho$.
Tribasic vanadic acid,	$\mathbf{V}OHo_3$.
Pyrovanadic acid,	$\mathbf{V}_2O_3Ho_4$.

Hypovanadous oxide, $'\mathbf{V}''_2O_2$, is formed when the vapor of the oxytrichloride, mixed with hydrogen, is passed through a red-hot tube:

$$\underset{\text{Vanadic oxytrichloride.}}{2\mathbf{V}OCl_3} + 3H_2 = \underset{\text{Hypovanadous oxide.}}{'\mathbf{V}''_2O_2} + \underset{\text{Hydrochloric acid.}}{6HCl.}$$

It is a gray powder, with a metallic lustre. Acids dissolve it, yielding a lavender-colored solution, which instantly becomes brown on exposure to the air.

Hypovanadous oxide was mistaken by Berzelius for metallic vanadium.

Vanadous oxide, $\mathbf{V}_2O_3$, remains behind as a black lustrous powder when vanadic anhydride is heated to redness in a current of hydrogen. Even at ordinary temperatures it slowly absorbs oxygen, forming hypovanadic oxide, $'\mathbf{V}^{iv}{}_2O_4$, and, when gently warmed in air, glows and is converted into vanadic anhydride. It is insoluble in acids.

Hypovanadic oxide, $'\mathbf{V}^{iv}{}_2O_4$, is formed as above by the spontaneous oxidation of vanadous oxide. It may also be obtained by fusing together equal molecular proportions of vanadous oxide and vanadic anhydride:

$$\underset{\text{Vanadous oxide.}}{\mathbf{V}_2O_3} + \underset{\text{Vanadic anhydride.}}{\mathbf{V}_2O_5} = \underset{\text{Hypovanadic oxide.}}{2'\mathbf{V}^{iv}{}_2O_4.}$$

It is a blue powder, consisting of minute shining crystals. When exposed to moist air it is slowly converted into an olive-green hydrate. Acids dissolve it with difficulty, yielding a blue solution.

Venadic anhydride, $\mathbf{V}_2O_5$.—Minerals containing vanadium are fused with nitre, and the mass is extracted with water. The solution, which contains an alkaline vanadate along with various impurities, is then almost neutralized with nitric acid and precipitated with baric chloride. The precipitate, consisting of baric vanadate and other barium salts, is decomposed by boiling with dilute sulphuric acid, and the solution, filtered from the baric sulphate, is neutralized with ammonia and evaporated to a small bulk, after which pieces of ammonic chloride are placed in the solution. This causes the ammonic metavanadate, which is very insoluble in a concentrated solution of ammonic chloride, to be deposited in small crystals. These are washed with a solution

of ammonic chloride, and decomposed by ignition in an open crucible, when pure vanadic anhydride remains behind.

Vanadic anhydride is a reddish-brown mass which melts at a red heat, and solidifies in a crystalline form on cooling. It is very slightly soluble in water, to which it imparts a yellowish tinge. Both acids and alkalies dissolve it readily. The acid solutions yield with reducing agents first a blue, and afterwards a green coloration.

Vanadates.—The various forms of vanadic acid are known only in their salts. The *orthovanadates* (or tribasic vanadates), the *metavanadates*, and the *pyrovanadates* are isomorphous with the corresponding compounds of phosphorus. In addition to these, a fourth series is known, the *tetravanadates*, of which *diammonic tetravanadate*, $\mathbf{V}_4O_9(NH_4O)_2,4\mathbf{O}H_2$, is an example:

Ammonic metavanadate, ...	$\mathbf{V}O_2(NH_4O)$.
Argentic orthovanadate, ...	$\mathbf{V}OAgo_3$.
Argentic pyrovanadate, ...	$\mathbf{V}_2O_3Ago_4$.
Vanadinite, ...	$\mathbf{V}_3O_3Pbo''_4\left(\begin{smallmatrix}O\\Cl\end{smallmatrix}Pb''\right)$.

ARSENIC, As_4.

Atomic weight = 75. *Molecular weight* = 300. *Molecular volume* $\square\square$. 1 *litre of arsenic vapor weighs* 150 *criths. Sp. gr.* 5.6 *to* 5.9. *Volatile at* 180° C. (356° F.). *Atomicity* ''' *and* v. *Evidence of atomicity:*

Arseniuretted hydrogen, ...	$\mathbf{As}'''H_3$.
Arsenious chloride, ...	$\mathbf{As}'''Cl_3$.
Tetrethylarsenic chloride, ...	$\mathbf{As}^{v}Et_4Cl$.

History.—Arsenic was known to the alchemists, but Brand, and later Scheele, first investigated its chemical nature.

Occurrence.—Arsenic is widely distributed in nature. It occurs both in the free state and in combination with various other metals in the form of ores. Of the latter the principal are: *realgar*, $'\mathbf{As}''_2S''_2$; *orpiment*, $\mathbf{As}_2S''_3$; *arsenical pyrites*, $'\mathbf{As}''_2(Fe_2S''_2)''_2$; and *arsenical iron*, $'\mathbf{As}''_2Fe^{iv}$. It is found in small quantities in other minerals, such as iron pyrites, for which reason sulphuric acid which has been manufactured from pyrites is generally contaminated with arsenic. In minute traces it occurs in some mineral waters, and in the water and mud of many rivers. It is also contained in coal-smoke (derived in this case from the pyrites of the coal), and consequently in the air of towns.

Preparation.—1. Arsenic is obtained by heating arsenical pyrites. The arsenic volatilizes and may be condensed, whilst ferrous sulphide remains behind:

$$\underset{\substack{\text{Ferroarsenious}\\ \text{sulphide.}}}{'\mathbf{As}''_2(Fe_2S''_2)''_2} = As_2 + \underset{\substack{\text{Ferrous}\\ \text{sulphide.}}}{4\mathbf{Fe}S''}.$$

2. It may also be prepared from arsenious anhydride, a substance produced in the roasting of many ores. The arsenious anhydride is reduced by heating with charcoal:

$$\underset{\substack{\text{Arsenious}\\ \text{anhydride.}}}{\mathbf{As}_2O_3} + 3C = 2As + \underset{\substack{\text{Carbonic}\\ \text{oxide.}}}{3\mathbf{C}O}.$$

Properties.—Arsenic, like phosphorus, is known in more than one form. When arsenic is sublimed in a current of hydrogen, it is deposited close to the heated portion of the tube in crystals, but further on, where the tube is colder, amorphous arsenic collects. The crystalline variety forms acute rhombohedra, with a steel-gray color and a metallic lustre, possessing a sp. gr. of 5.727. In dry air it may be preserved without change, but in presence of moisture it becomes coated with a blackish-gray crust due to oxidation. When heated under ordinary pressure, it volatilizes without fusing; but by inclosing it in a sealed tube, so as to subject it to the pressure of its own vapor, it may be fused. The vapor is lemon-colored, and possesses an odor of garlic. The molecular weight of arsenic, as deduced from the vapor-density, is 300, showing that the molecule of this element is, like that of phosphorus, tetratomic. At the highest temperature at which the vapor-density of arsenic has been determined (yellow heat), a partial dissociation is, however, found to have occurred, and the value for the vapor-density lies between those required for As_2 and As_4 (Victor Meyer).

The amorphous variety forms a black mass with a vitreous lustre. Its sp. gr. is 4.71. When heated to 360° C. (680° F.) it is converted into the crystalline or metallic variety, great heat being liberated in the transformation. It is much more permanent in air than crystalline arsenic. Amorphous arsenic may also be obtained as a gray powder. This variety is deposited in the coldest parts of the tube during the sublimation in hydrogen.

Reactions.—1. When heated in air or oxygen arsenic burns, forming arsenious anhydride. In like manner, when arsenic is treated with oxidizing agents, arsenious anhydride and arsenic acid are produced.

2. When finely-divided arsenic is introduced into chlorine, it inflames spontaneously, yielding arsenious chloride.

It also combines directly with most of the other elements.

Use.—A small quantity of arsenic is added to the lead which is used in the manufacture of shot, as it is found that this addition enables the metal more readily to assume the spherical form, and at the same time renders it harder.

COMPOUND OF ARSENIC WITH HYDROGEN.

ARSENIURETTED HYDROGEN, *Arsenious Hydride.*

$$\mathbf{AsH_3}.$$

Molecular weight = 78. *Molecular volume* $\square\square$. 1 *litre weighs* 39 *criths. Boils at* —40° C. (—40° F.).

Preparation.—1. This gas is obtained in the pure state by the action of dilute sulphuric or hydrochloric acid on an alloy of arsenic and zinc:

$$\underset{\text{Arsenious zincide.}}{As_2Zn''_3} + \underset{\text{Sulphuric acid.}}{3SO_2Ho_2} = \underset{\text{Zincic sulphate.}}{3SO_2Zno''} + \underset{\text{Arseniuretted hydrogen.}}{2AsH_3}.$$

2. It is formed by the action of nascent hydrogen upon soluble arsenic compounds: thus by the introduction of arsenious acid into an apparatus evolving hydrogen from zinc and sulphuric acid:

$$\underset{\text{Arsenious acid.}}{AsHo_3} + 3H_2 = \underset{\text{Arseniuretted hydrogen.}}{AsH_3} + \underset{\text{Water.}}{3OH_2}.$$

In this case the gas is mixed with an excess of hydrogen.

Properties.—Arseniuretted hydrogen is a colorless gas of a very disagreeable odor. At —40° C. it condenses to a colorless and transparent liquid which does not solidify at —100° C. (—148° F.). Water dissolves it but slightly. It is devoid of basic properties.

It is one of the most poisonous substances known. Gehlen, of Göttingen, lost his life by incautiously smelling a leaky joint of an apparatus in which he was preparing the gas, in order to detect the escape.

Reactions.—1. When burnt with free access of air it forms water and arsenious anhydride:

$$\underset{\text{Arseniuretted hydrogen.}}{2AsH_3} + 3O_2 = \underset{\text{Arsenious anhydride.}}{As_2O_3} + \underset{\text{Water.}}{3OH_2}.$$

2 When burnt with a limited supply of air, it yields water and free arsenic:

$$\underset{\text{Arseniuretted hydrogen.}}{4AsH_3} + 3O_2 = As_4 + \underset{\text{Water.}}{6OH_2}.$$

Thus if a piece of white porcelain be held in the flame of arseniuretted hydrogen burning in air, a black shining spot of metallic arsenic is deposited on the porcelain.

3. When exposed to a low red heat, it is decomposed into arsenic and hydrogen. This reaction, coupled with the formation of arseniuretted hydrogen by the action of nascent hydrogen on soluble compounds of arsenic, is employed as a means of detecting minute traces of this element. (See *Marsh's Test, Reactions of Arsenic.*)

4. When passed through a solution of argentic nitrate, it yields a precipitate of metallic silver, whilst arsenious and nitric acids remain in solution:

$$\underset{\text{Argentic nitrate.}}{6NO_2Ago} + \underset{\text{Water.}}{3OH_2} + \underset{\text{Arseniuretted hydrogen.}}{AsH_3} = \underset{\text{Nitric acid.}}{6NO_2Ho} + \underset{\text{Arsenious acid.}}{AsHo_3} + 3Ag_2.$$

COMPOUNDS OF ARSENIC WITH THE HALOGENS.

ARSENIOUS CHLORIDE.

$\mathbf{As}Cl_3.$

Atomic weight = 181.5. *Molecular volume* $\square\square$. 1 *litre of arsenious chloride vapor weighs* 90.75 *criths*. *Sp. gr.* 2.205. *Boils at* 134° C.

Preparation.—1. Arsenious chloride is obtained by the action of dry chlorine on arsenic. The product must be left in contact with arsenic, in order to free it from excess of chlorine, and then rectified.

2. It may also be prepared by distilling arsenic with corrosive sublimate:

$$\mathbf{As}_2 + \underset{\text{Mercuric chloride.}}{6\mathbf{Hg}Cl_2} = \underset{\text{Mercurous chloride.}}{3'\mathbf{Hg}'_2Cl_2} + \underset{\text{Arsenious chloride.}}{2\mathbf{As}Cl_3.}$$

3. It is most readily obtained by distilling a mixture of arsenious anhydride, sodic chloride, and concentrated sulphuric acid:

$$\underset{\text{Arsenious anhydride.}}{\mathbf{As}_2O_3} + \underset{\text{Sodic chloride.}}{6NaCl} + \underset{\text{Sulphuric acid.}}{6\mathbf{S}O_2Ho_2} = \underset{\text{Arsenious chloride.}}{2\mathbf{As}Cl_3}$$

$$+ \underset{\text{Hydric sodic sulphate.}}{6\mathbf{S}O_2HoNao} + \underset{\text{Water.}}{3\mathbf{O}H_2.}$$

In this way hydrochloric acid, in the preparation of which arsenical sulphuric acid has been employed, always contains arsenic.

4. When a solution of arsenious anhydride in aqueous hydrochloric acid is boiled, arsenious chloride volatilizes along with the steam:

$$\underset{\text{Arsenious anhydride.}}{\mathbf{As}_2O_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Arsenious chloride.}}{2\mathbf{As}Cl_3} + \underset{\text{Water.}}{3\mathbf{O}H_2.}$$

Properties.—Arsenious chloride is an oily liquid which does not solidify at —29° C. It fumes strongly in contact with moist air. It is extremely poisonous.

Reactions.—1. A small quantity of water dissolves it, forming a clear solution, from which needle-shaped crystals of arsenious chlordihydrate are deposited on standing:

$$\underset{\text{Arsenious chloride.}}{\mathbf{As}Cl_3} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Arsenious chlordihydrate.}}{\mathbf{As}ClHo_2} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

2. An excess of water decomposes it into arsenious anhydride and hydrochloric acid:

$$\underset{\text{Arsenious chloride.}}{2\mathbf{As}Cl_3} + \underset{\text{Water.}}{3\mathbf{O}H_2} = \underset{\text{Hydrochloric acid.}}{6HCl} + \underset{\text{Arsenious anhydride.}}{\mathbf{As}_2O_3}.$$

3. It absorbs gaseous ammonia, forming a crystalline compound of the formula $\mathbf{As}Cl_3,2\mathbf{N}H_3$.

ARSENIOUS BROMIDE, $\mathbf{As}Br_3$ (*molecular volume* $\square\square$), is prepared by adding finely powdered arsenic to a solution of bromine in carbonic disulphide. It crystallizes in colorless deliquescent prisms, fusing between 20° and 25° C. (68–77° F.). It boils at 220° C. (428° F.). Water decomposes it like the chloride.

ARSENIOUS IODIDE, $\mathbf{As}I_3$ (*molecular volume* $\square\square$), is prepared in a similar manner, and forms lustrous brick-red laminæ.

ARSENIOUS FLUORIDE, $\mathbf{As}F_3$ (*molecular volume* $\square\square$), is obtained by distilling a mixture of 1 part of powdered fluorspar and 1 part of arsenious anhydride with 5 parts of concentrated sulphuric acid:

$$\mathbf{As}_2O_3 + 6HF = 2\mathbf{As}F_3 + 3\mathbf{O}H_2.$$

It is a colorless fuming liquid of sp. gr. 2.7, boiling at 63° C. (145° F.). Brought in contact with the skin it produces very dangerous wounds. Water decomposes it like arsenious chloride.

ARSENIC PENTAFLUORIDE, $\mathbf{As}F_5$, is known only in the form of the double compound, $\mathbf{As}F_5,KF$, obtained by dissolving potassic arsenate in hydrofluoric acid.

COMPOUNDS OF ARSENIC WITH OXYGEN AND HYDROXYL.

Arsenious anhydride, ...	$(\mathbf{As}_2O_3)_2$.
Arsenic anhydride, ...	$\mathbf{As}_2O_5$.
Arsenious acid, ...	$\mathbf{As}Ho_3$.
Arsenic acid, ...	$\mathbf{As}OHo_3$.

ARSENIOUS ANHYDRIDE, *Arsenic, White Arsenic, White Oxide of Arsenic.*

$$(\mathbf{As}_2O_3)_2.$$

Molecular weight = 396. *Molecular volume* $\square\square$. 1 *litre of arsenious anhydride vapor weighs* 198 *criths. Sp. gr.* (*octahedral*) 3.69, (*amorphous*) 3.74.

Occurrence.—Arsenious anhydride is found in nature in two rare minerals: in the octahedral form as arsenic bloom and in rhombic crystals as claudetite.

Preparation.—It is formed when arsenic is burnt in air or oxygen. In this way, it is obtained as a by-product in the roasting of arsenical ores in various metallurgical operations. The arsenious anhydride sublimes and is condensed in large flues.

Properties.—Commercial amorphous arsenious anhydride forms, when first prepared, a colorless vitreous mass, which after a time becomes

white and opaque, owing to its gradual transformation into the crystalline variety. This change is accompanied by a decrease in the sp. gr. from 3.74 to 3.69. Crystalline arsenious anhydride is soluble in 80 parts of cold water; the amorphous modification in 25 parts; hydrochloric acid increases the solubility. The hot saturated solution in hydrochloric acid deposits octahedral crystals; if a solution of the amorphous variety be employed, the formation of each crystal is attended with a flash of light visible in the dark. When the octahedral anhydride is heated, it sublimes without fusing, and is again condensed in octahedral crystals; under pressure, however, it may be fused, and is thus converted into the amorphous modification.

A second crystalline modification of arsenious anhydride, belonging to the rhombic system, is sometimes found in the arsenic flues. It is also deposited from a solution of an excess of the anhydride in boiling caustic potash, or from a solution of argentic arsenite in nitric acid.

Arsenious anhydride has a faint, sweetish metallic taste, and, when taken internally, acts as an irritant poison. A dose of 0.06 gram has been known to prove fatal. The best antidote is *freshly prepared* ferric hydrate ($'\mathbf{Fe}'''_2Ho_6$), which must be administered in a large dose as soon as possible after the poison has been swallowed. The arsenious acid is oxidized by the ferric hydrate to arsenic acid, which combines with the excess of ferric hydrate to form a basic ferric arsenate, insoluble in water and in the liquids of the stomach. By keeping, the ferric hydrate becomes crystalline and inactive: it is therefore prepared, when wanted, by adding calcined magnesia to a solution of ferric chloride or sulphate:

$$\underset{\text{Ferric chloride.}}{'\mathbf{Fe}'''_2Cl_6} + \underset{\text{Magnesia.}}{3\mathbf{Mg}O} + \underset{\text{Water.}}{3OH_2} = \underset{\text{Ferric hydrate.}}{'\mathbf{Fe}'''_2Ho_6} + \underset{\text{Magnesic chloride.}}{3\mathbf{Mg}Cl_2}.$$

The magnesic chloride, which is simultaneously formed in this reaction, serves by its aperient action to remove the various matters as speedily as possible from the stomach.

In spite of the poisonous properties of arsenious anhydride, it is possible by long use to train the system to support relatively large doses of this substance. In Styria, the practice of arsenic eating is stated to be not uncommon. An arsenic eater has been known to consume 0.3 gram of arsenious anhydride at once without perceptible ill-effect. The practice is asserted by the arsenic eaters to improve the complexion and to prevent shortness of breath.

Uses.—Arsenious anhydride is employed in the preparation of arsenical pigments and in the manufacture of glass.

ARSENIOUS ACID.

$AsHo_3$.

Molecular weight = 126.

When arsenious anhydride is dissolved in water the solution reddens litmus feebly, and contains arsenious acid. This acid cannot however

be isolated, since on concentration the solution deposits crystals of the anhydride.

Arsenites.—There are two classes of arsenites: the ortharsenites, derived from the acid $\mathbf{As}Ho_3$; and the metarsenites, derived from the acid $\mathbf{As}OHo$. Only the arsenites of the alkali-metals are soluble in water. They yield with argentic nitrate a yellow precipitate of triargentic arsenite, $\mathbf{As}Ago_3$. Among the arsenites important by their uses, may be mentioned *dihydric potassic arsenite*, $\mathbf{As}Ho_2Ko$, employed in medicine under the name of *Fowler's solution;* and *hydric cupric arsenite*, $\mathbf{As}HoCuo''$, which forms the pigment *Scheele's green*. *Schweinfurt green*, a double metarsenite and acetate of copper of the formula

$$3\mathbf{As}_2O_2Cuo'',\mathbf{Cu}(C_2H_3O_2)_2,$$

is prepared by boiling arsenious acid with cupric acetate.

ARSENIC ANHYDRIDE.

$$\mathbf{As}_2O_5.$$

Molecular weight = 230.

Preparation.—This compound is obtained by heating arsenic acid nearly to redness:

$$\underset{\text{Arsenic acid.}}{2\mathbf{As}OHo_3} = \underset{\text{Water.}}{3\mathbf{O}H_2} + \underset{\text{Arsenic anhydride.}}{\mathbf{As}_2O_5}.$$

Properties.—It forms a white porous mass.

Reactions.—1. It dissolves in water with formation of arsenic acid.

2. When heated to bright redness it fuses and is decomposed into arsenious anhydride and oxygen.

3. With gaseous hydrochloric acid it yields, even at ordinary temperatures, arsenious trichloride, chlorine, and water:

$$\underset{\text{Arsenic anhydride.}}{\mathbf{As}_2O_5} + \underset{\text{Hydrochloric acid.}}{10HCl} = \underset{\text{Arsenious trichloride.}}{2\mathbf{As}Cl_3} + 2Cl_2 + \underset{\text{Water.}}{5\mathbf{O}H_2}.$$

ARSENIC ACID.

$$\mathbf{As}OHo_3.$$

Molecular weight = 142.

Preparation.—Arsenic acid is prepared by treating arsenious anhydride with nitric acid:

$$\mathbf{As}_2O_3 + 2\mathbf{N}O_2Ho + 2\mathbf{O}H_2 = 2\mathbf{As}OHo_3 + \mathbf{N}_2O_3.$$

Properties.—When a solutien of arsenic acid is evaporated to a syrup, and then cooled below 15° C. (59° F.), crystals of the formula $2\mathbf{As}OHo_3,\mathbf{O}H_2$ are deposited. These crystals part with their water of crystallization at 100° C., and are converted into ortharsenic acid, $\mathbf{As}OHo_3$. When this acid is heated to 180° C. (356° F.) it fuses and gives off water, and on cooling, hard shining prismatic crystals of pyrarsenic acid, $\mathbf{As}_2O_3Ho_4$, separate out. If the heating be carried to 206° C. (403° F.), the whole is converted into a white nacreous mass of metarsenic acid, $\mathbf{As}O_2Ho$. These three acids correspond to the three varieties of phosphoric acid; but the pyro- and metarsenic acids differ from the pyro- and meta-phosphoric acids in being capable of existing only in the solid state. In solution they are at once converted into ortharsenic acid, and the same is the case with their salts, which may be prepared in the same way as the corresponding salts of meta- and pyro-phosphoric acid (pp. 354 and 355).

Reactions.—1. When arsenic acid is distilled with fuming hydrochloric acid, arsenious trichloride, chlorine, and water distil over:

$$\underset{\text{Arsenic acid.}}{\mathbf{As}OHo_3} + 5HCl = \underset{\text{Arsenious trichloride.}}{\mathbf{As}Cl_3} + Cl_2 + \underset{\text{Water.}}{4\mathbf{O}H_2}.$$

In the receiver the reverse reaction takes place, arsenic acid and hydrochloric acid being regenerated.

2. Sulphurous acid reduces it to arsenious acid:

$$\underset{\text{Arsenic acid.}}{\mathbf{As}OHo_3} + \underset{\text{Sulphurous acid.}}{\mathbf{S}OHo_2} = \underset{\text{Arsenious acid.}}{\mathbf{As}Ho_3} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2}.$$

Other reducing agents act in a similar manner.

Arsenates.—The arsenates are isomorphous with the corresponding phosphates. Arsenic acid is a tribasic acid, and forms three series of salts; normal, monohydric, and dihydric. The alkaline arsenates are soluble in water; of the others only the dihydric salts are soluble, but all dissolve readily in acids.

The following arsenates occur in nature:

Haidingerite, ...	$2\mathbf{As}OHoCao'',\mathbf{O}H_2$.
Pharmacolite, ...	$2\mathbf{As}OHoCao'',5\mathbf{O}H_2$.
Cobalt bloom, ...	$\mathbf{As}_2O_2Coo''_3,8\mathbf{O}H_2$.
Mimetesite (isomorphous with pyromorphite, vanadinite, and apatite, pp. 357 and 366), . .	$\mathbf{As}_3O_3Pbo'''_4\left(\begin{matrix}O\\Cl\end{matrix}Pb''\right)$.

For the reactions of the arsenates, see *General Reactions of Arsenic.*

COMPOUNDS OF ARSENIC WITH SULPHUR AND HYDROSULPHYL.

Realgar, ...	$\left\{\begin{array}{l}\mathbf{As}S''\\\mathbf{As}S''\end{array}\right. = {}'\mathbf{As}''_2S''_2.$
Sulpharsenious anhydride (*Arsenious sulphide*), ...	$\mathbf{As}_2S''_3.$
Sulpharsenic anhydride (*Arsenic sulphide*), ...	$\mathbf{As}_2S''_5.$
Sulpharsenious acid, ...	$\mathbf{As}Hs_3.$
Sulpharsenic acid, ...	$\mathbf{As}S''Hs_3.$

DIARSENIOUS DISULPHIDE, *Realgar.*

$$'\mathbf{As}''_2S''_2, \text{ or } \left\{\begin{array}{l}\mathbf{As}S''\\\mathbf{As}S''.\end{array}\right.$$

Molecular weight = 214. *Sp. gr.* 3.5.

Occurrence.—This substance occurs in nature as the mineral *realgar.*

Preparation.—1. It may be obtained artificially by heating together sulphur and arsenic in the proportions expressed by the formula.

2. A second method consists in heating in an iron retort a mixture of arsenical pyrites and iron pyrites:

$$\underset{\substack{\text{Arsenical}\\\text{pyrites.}}}{'\mathbf{As}''_2(Fe_2S''_2)''_2} + \underset{\substack{\text{Ferric}\\\text{disulphide.}}}{2\mathbf{Fe}S''_2} = \underset{\substack{\text{Diarsenious}\\\text{disulphide.}}}{'\mathbf{As}''_2S''_2} + \underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{6\mathbf{Fe}S''.}$$

The diarsenious disulphide distils over, whilst ferrous sulphide remains in the retort. Most of the realgar of commerce is prepared by this method.

Properties.—Native realgar occurs in ruby-colored monoclinic prisms and also massive. The artificial product forms a dark-red crystalline mass. It fuses readily and may be distilled without decomposition.

Reaction.—1. When heated in contact with air it burns with formation of arsenious and sulphurous anhydrides:

$$\underset{\substack{\text{Diarsenious}\\\text{disulphide.}}}{'\mathbf{As}''_2S''_2} + 7O = \underset{\substack{\text{Arsenious}\\\text{anhydride.}}}{\mathbf{As}_2O_3} + \underset{\substack{\text{Sulphurous}\\\text{anydride.}}}{2\mathbf{S}O_2.}$$

SULPHARSENIOUS ANHYDRIDE, *Arsenious Sulphide, Orpiment.*

$$\mathbf{As}_2S''_3.$$

Molecular weight = 246. *Sp. gr.* 3.5.

Occurrence.—Sulpharsenious anhydride occurs native as the mineral *orpiment.*

Preparation.—It may be obtained by precipitating a solution of arsenious anhydride in hydrochloric acid with sulphuretted hydrogen:

$2AsCl_3$	+	$3SH_2$	=	$6HCl$	+	$As_2S''_3$.
Arsenious chloride.		Sulphuretted hydrogen.		Hydrochloric acid.		Arsenious sulphide.

Properties.—Native orpiment forms lemon-colored rhombic prisms. The substance obtained by precipitation is a yellow powder, which fuses to a reddish liquid, and may be distilled without decomposition.

Reactions.—1. Arsenious sulphide dissolves in caustic alkalies, producing an arsenite and a sulpharsenite:

$As_2S''_3$	+	$4OKH$	=	$AsHoKo_2$	+	$AsHsKs_2$	+	OH_2.
Arsenious sulphide.		Potassic hydrate.		Hydric dipotassic arsenite.		Sulphydric disulphopotassic sulpharsenite.		Water.

By the addition of an acid the arsenious sulphide is reprecipitated:

$AsHoKo_2$	+	$AsHsKs_2$	+	$4HCl$	=	$4KCl$
Hydric dipotassic arsenite.		Sulphydric disulphopotassic sulpharsenite.		Hydrochloric acid.		Potassic chloride.

+	$As_2S''_3$	+	$3OH_2$.
	Arsenious sulphide.		Water.

2. It dissolves in alkaline sulphides, forming sulpharsenites:

$As_2S''_3$	+	$3SK_2$	=	$2AsKs_3$.
Arsenious sulphide.		Potassic sulphide.		Potassic sulpharsenite.

Sulpharsenites.—These salts correspond to the arsenites. Only the alkaline salts are soluble. On the addition of an acid to their solutions arsenious sulphide is precipitated, and sulphuretted hydrogen is evolved:

$2AsKs_3$	+	$6HCl$	=	$6KCl$	+	$As_2S''_3$	+	$3SH_2$.
Potassic sulpharsenite.		Hydrochloric acid.		Potassic chloride.		Arsenious sulphide.		Sulphuretted hydrogen.

Colloidal Arsenious Sulphide.—On saturating a pure aqueous solution of arsenious anhydride with sulphuretted hydrogen, the liquor assumes a yellow color with a reddish fluorescence; but no precipitate is formed. In this condition the solution contains a colloidal modification of arsenious sulphide, which may be separated from unaltered arsenious anhydride by dialysis. By spontaneous evaporation this soluble sulphide is obtained in transparent amorphous masses of a yellow or reddish-yellow color with a conchoidal fracture. Acids and various metallic salts precipitate ordinary insoluble arsenious sulphide from the solution.

SULPHARSENIC ANHYDRIDE, *Arsenic Sulphide.*

$$\mathbf{As}_2S''_5.$$

Molecular weight = 310.

Preparation.—1. Sulpharsenic anhydride may be prepared by fusing together arsenious sulphide and sulphur in the required atomic proportions.

2. It is obtained as a yellow precipitate by adding hydrochloric acid to a solution of a sulpharsenate:

$$\underset{\text{Potassic sulpharsenate.}}{2\mathbf{As}S''Ks_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Potassic chloride.}}{6KCl} + \underset{\text{Arsenic sulphide.}}{\mathbf{As}_2S''_5} + \underset{\text{Sulphuretted hydrogen.}}{3SH_2}.$$

It cannot, as was formerly supposed, be prepared by passing sulphuretted hydrogen through a solution of arsenic acid. The yellow precipitate formed under these circumstances is a mixture of arsenious sulphide and sulphur in the proportion $\mathbf{As}_2S''_3 + S_2$.

Sulpharsenates.—These salts may be prepared by passing sulphuretted hydrogen through solutions of arsenates:

$$\underset{\text{Hydric disodic arsenate.}}{\mathbf{As}OHoNao_2} + \underset{\text{Sulphuretted hydrogen.}}{4\mathbf{S}H_2} = \underset{\text{Sulphydric disulphosodic sulpharsenate.}}{\mathbf{As}S''HsNas_2} + \underset{\text{Water.}}{4\mathbf{O}H_2}.$$

General Properties and Reactions of the Compounds of Arsenic.—Owing to the frequency of cases of poisoning, both accidental and intentional, with arsenic, the detection of this substance, even when present in the minutest traces, becomes a matter of great importance. For a detailed account of the methods to be employed and of the precautions to be taken, in a toxicological investigation of this kind, special works on analytical chemistry must be consulted.

a. Arsenites.—From the hydrochloric acid solution of an arsenite or of arsenious anhydride, *sulphuretted hydrogen* precipitates yellow arsenious sulphide. The precipitate is formed slowly in the cold, more rapidly on warming; it is soluble in ammonic sulphide, caustic alkalies, ammonic carbonate, and hydric potassic sulphite; almost insoluble in hydrochloric acid. Soluble arsenites yield in neutral solution with *argentic nitrate* a yellow precipitate of argentic arsenite, soluble both in nitric acid and in ammonia. With a solution of arsenious anhydride the yellow precipitate only makes its appearance on the careful addition of ammonia, so as to neutralize the free nitric acid.

b. Arsenates.—Only the alkaline arsenates are soluble in water. From neutral solutions *argentic nitrate* precipitates reddish-brown triargentic arsenate, soluble in ammonia. A mixture of magnesic sulphate, ammonic chloride, and ammonia gives a white crystalline precipitate of ammonic magnesic arsenate ($\mathbf{As}OMgo''Amo,6\mathbf{O}H_2$), isomorphous with the corresponding phosphorous compound (p. 357). *Sulphuretted hydro-*

gen in acid solutions first reduces the arsenic acid to arsenious acid with separation of sulphur; after which the arsenious acid is precipitated as arsenious sulphide. In the cold, the reduction of arsenic acid by sulphuretted hydrogen takes place with extreme slowness; the action is greatly aided by keeping the liquid at a temperature of from 50° to 70° C. (122–158° F.) while passing in the sulphuretted hydrogen.

Marsh's Test.—If any of the oxygen or halogen compounds of arsenic be introduced into an apparatus in which hydrogen is being generated from zinc and dilute sulphuric acid, the arsenic is evolved as arseniuretted hydrogen together with an excess of hydrogen. If the escaping gas be ignited and a cold surface of white porcelain be held in the flame, a black lustrous film of metallic arsenic is deposited upon the porcelain. In like manner, if the gas be passed through a strongly heated glass tube, metallic arsenic condenses as a lustrous mirror just beyond the heated portion. These thin films of arsenic are at once dissolved by a solution of sodic hypochlorite. (Distinction from antimony.) The sulphur compounds of arsenic, and metallic arsenic itself, do not yield arseniuretted hydrogen under the above conditions. The presence of nitric acid and other oxidizing agents prevents the formation of arseniuretted hydrogen. In applying Marsh's test, and all similar tests, it is necessary to ascertain by a blank experiment that the reagents employed are free from arsenic.

Reinsch's Test.—If a solution of an arsenic compound in hydrochloric acid be boiled with a piece of pure bright copper, the surface of the metal becomes covered with a dark-gray coating of arsenide of copper. If this coating be separated, dried, and then heated in a small glass tube, a portion of the arsenic is oxidized to arsenious anhydride, which forms a sublimate of minute transparent octahedra in the tube. To this sublimate the above confirmatory tests may be applied. This test ought never to be trusted when the mixture contains a chlorate or a nitrate, as a portion of the copper will then be dissolved, and the traces of arsenic which are generally present in the purest copper will be precipitated on the remaining copper.

All compounds of arsenic, when heated in a narrow bulb-tube with a mixture of sodic carbonate and potassic cyanide, are reduced to metallic arsenic, which sublimes and collects as a mirror in the colder part of the tube. When heated with sodic carbonate on charcoal in the reducing flame of the blowpipe, the arsenic compounds evolve a characteristic odor of garlic.

NIOBIUM, Nb, and **TANTALUM**, Ta.

Atomic weights: Nb = 94, Ta = 182. *Atomicity* ''' *and* $^{\mathrm{v}}$.

Occurrence.—These two very rare elements generally occur together as tantalates and niobates.

Preparation.—Very little is known of them in the free state. They may be obtained as black powders by heating potassic niobofluoride and potassic tantalofluoride with potassium or sodium.

The following are some of the principal compounds of these elements:

COMPOUNDS OF NIOBIUM.

Niobic chloride, ...	$NbCl_5$.
Niobic oxytrichloride, ...	$NbOCl_3$.
Niobic fluoride, ...	NbF_2.
Potassic niobofluoride, ...	NbK_2F_7.
Hyponiobous oxide, ...	$'Nb''_2O_2$.
Hyponiobic oxide, ...	$'Nb^{iv}_2O_4$.
Niobic anhydride, ...	Nb_2O_5.

COMPOUNDS OF TANTALUM.

These correspond with the above compounds of niobium, with the single exception that hypotantalous oxide has not been prepared.

ANTIMONY, Sb_4?

Atomic weight = 120. *Probable molecular weight* = 480. *Sp. gr.* (*crystalline*) 6.7, (*amorphous*) 5.78. *Fuses at* 430° C. (806° F.). *Atomicity* ''' *and* v. *Evidence of atomicity:*

Antimonious chloride, ...	$Sb'''Cl_3$.
Antimonic tetretho-chloride (*tetrethyl stibonic chloride*), ...	Sb^vEt_4Cl.
Antimonic chloride, ...	Sb^vCl_5.

History.—Many of the compounds of antimony have been known from very early times. In the fifteenth century Basil Valentine described the preparation of metallic antimony.

Occurrence.—Antimony is rarely found native. Sometimes it occurs alloyed with other metals in various minerals. Combined with oxygen, it occurs as *valentinite* or antimonious oxide, and as *antimony ochre* or diantimonious tetroxide. The chief source of antimony is gray antimony ore or *stibnite*, which consists of antimonious sulphide. Sulphantimonites also occur, such as *miargyrite*, an argentic meta-sulphantimonite.

a. Crystalline Antimony.

Preparation.—1. Antimony may be obtained by fusing the powdered native sulphide with iron filings:

$$\underset{\text{Antimonious sulphide.}}{Sb_2S''_3} + 3Fe = \underset{\text{Ferrous sulphide.}}{3FeS''} + 2Sb.$$

2. In preparing antimony on a large scale, the sulphide is first roasted in contact with air, when it is partially converted into antimonious oxide:

$$\underset{\text{Antimonious sulphide.}}{2Sb_2S''_3} + 9O_2 = \underset{\text{Antimonious oxide.}}{2Sb_2O_3} + \underset{\text{Sulphurous anhydride.}}{6SO_2}.$$

The roasted mineral is then fused with charcoal and sodic carbonate. The reaction takes place in two stages: first, the remaining sulphide is converted into oxide by the sodic carbonate, and subsequently the oxide is reduced by the carbon:

$$1.\ \mathbf{Sb}_2\mathrm{S''}_3 + 3\mathbf{C}\mathrm{ONao}_2 = 3\mathbf{C}\mathrm{O}_2 + 3\mathbf{S}\mathrm{Na}_2 + \mathbf{Sb}_2\mathrm{O}_3.$$

Antimonious sulphide. Sodic carbonate. Carbonic anhydride. Sodic sulphide. Antimonious oxide.

$$2.\ \mathbf{Sb}_2\mathrm{O}_3 + 3\mathrm{C} = 3\mathbf{C}\mathrm{O} + \mathrm{Sb}_2.$$

Antimonious oxide. Carbonic oxide.

3. Pure antimony may be obtained by reducing with charcoal the oxide formed by the action of nitric acid upon crude antimony.

Properties.—Antimony is a bluish-white lustrous metal, with a crystalline fracture. By slow cooling it may be obtained in rhombohedra, closely approximating to the cube. It fuses at 430° C., and may be distilled at a white heat.

β. *Amorphous Antimony.*

Preparation.—This variety, discovered by Gore (*Phil. Trans.*, 1858, p. 185), is obtained by the electrolysis of a solution of tartar emetic in antimonious chloride.

Properties.—Amorphous antimony has the appearance and lustre of polished steel, with a peculiar mammillated surface, and an amorphous fracture. It contains 5 or 6 per cent. of antimonious chloride derived from the electrolyte. When heated or struck it undergoes a molecular change, which spreads rapidly through the entire mass and is attended with a rise of temperature from 15° to 250° C. At the same time fumes of antimonious chloride are evolved. After this change the metal is found to possess an increased density and to have acquired a granular fracture.

Reactions.—1. When antimony is heated to redness in air it burns, forming antimonious oxide. If a small quantity of antimony be heated on charcoal to its point of ignition, and then thrown on to a large sheet of paper folded into the form of a tray, the metal breaks up into a number of globules, which dance about on the surface of the paper, burning brilliantly, and leaving black intermittent streaks behind them.

2. With hot concentrated sulphuric acid it yields antimonious sulphate with evolution of sulphurous anhydride:

$$2\mathrm{Sb} + 6\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2 = \mathbf{S}_3\mathrm{O}_6(\mathrm{Sb}_2\mathrm{O}_6)^{\mathrm{vi}} + 3\mathbf{S}\mathrm{O}_2 + 6\mathbf{O}\mathrm{H}_2.$$

Sulphuric acid. Antimonious sulphate. Sulphurous anhydride. Water.

Uses.—Metallic antimony is employed only in the form of its alloys, to which it imparts the valuable property of expanding on solidification. This renders them especially suitable for taking sharp casts. The most important alloys containing antimony are *type metal* and *Britannia metal* (*q.v.*).

COMPOUND OF ANTIMONY WITH HYDROGEN.

ANTIMONIURETTED HYDROGEN, *Antimonious Hydride.*

$$SbH_3.$$

Molecular weight = 123.

This compound is unknown in the pure condition.

Preparation.—1. It is prepared by the action of hydrochloric acid upon an alloy of zinc and antimony:

$$\underset{\text{Antimonious zincide.}}{Sb_2Zn''_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Antimonious hydride.}}{2SbH_3} + \underset{\text{Zincic chloride.}}{3ZnCl_2}.$$

2. It is formed by the action of nascent hydrogen, evolved from zinc and sulphuric acid, upon soluble antimony compounds:

$$\underset{\text{Antimonious chloride.}}{SbCl_3} + 3H_2 = \underset{\text{Antimonious hydride.}}{SbH_3} + 3HCl.$$

In both these reactions the antimonious hydride is always mixed with much hydrogen.

Properties.—It is a colorless gas, possessing a most offensive odor. It burns with a bluish flame.

Reactions.—1. When burnt in air or oxygen it yields water and antimonious oxide:

$$\underset{\text{Antimonious hydride.}}{2SbH_3} + 3O_2 = \underset{\text{Antimonious oxide.}}{Sb_2O_3} + \underset{\text{Water.}}{3OH_2}.$$

2. When burnt with a limited supply of air, the hydrogen alone is oxidized, the antimony being deposited:

$$4SbH_3 + 3O_2 = Sb_4 + 6OH_2.$$

Thus, if a cold surface of porcelain be held in the flame of antimonious hydride, a dull black spot of metallic antimony is formed.

3. When passed through a red-hot tube, it is decomposed, like arsenious hydride, into its elements.

4. When transmitted through a solution of argentic nitrate, it produces a black precipitate of antimonious argentide, thus differing from arsenious hydride (p. 368):

$$\underset{\text{Argentic nitrate.}}{3NO_2Ago} + \underset{\text{Antimonious hydride.}}{SbH_3} = \underset{\text{Nitric acid.}}{3NO_2Ho} + \underset{\text{Antimonious argentide.}}{SbAg_3}.$$

From the composition of this compound, and from that of some of its analogues, the composition of antimonious hydride is inferred.

Antimonious hydride,	$\mathbf{Sb}H_3$.
Antimonious bromide,	$\mathbf{Sb}Br_3$.
Antimonious argentide,	$\mathbf{Sb}Ag_3$.
Antimonious zincide,	$\mathbf{Sb}_2Zn''_3$.
Antimonious ethide (*Triethylstibine*),	$\mathbf{Sb}Et_3$.
Antimonious amylide (*Triamylstibine*),	$\mathbf{Sb}Ay_3$.

COMPOUNDS OF ANTIMONY WITH THE HALOGENS.

Antimonious chloride,	$\mathbf{Sb}Cl_3$.
Antimonic chloride,	$\mathbf{Sb}Cl_5$.
Antimonious bromide,	$\mathbf{Sb}Br_3$.
Antimonious iodide,	$\mathbf{Sb}I_3$.
Antimonious fluoride,	$\mathbf{Sb}F_3$.
Antimonic fluoride,	$\mathbf{Sb}F_5$.

ANTIMONIOUS CHLORIDE.

$\mathbf{Sb}Cl_3$.

Molecular weight = 226.5. *Molecular volume* $\square\square$. 1 *litre of antimonious chloride vapor weighs* 113.25 *criths. Fuses at* 72° C. (161.6° F.). *Boils at* 223° C. (433.4° F.).

Preparation.—1. This compound is formed when chlorine is passed over excess of metallic antimony or antimonious sulphide:

$$2\mathrm{Sb} + 3\mathrm{Cl}_2 = \underset{\text{Antimonious chloride.}}{2\mathbf{Sb}\mathrm{Cl}_3}.$$

$$\underset{\text{Antimonious sulphide.}}{2\mathbf{Sb}_2\mathrm{S}''_3} + 9\mathrm{Cl}_2 = \underset{\text{Antimonious chloride.}}{4\mathbf{Sb}\mathrm{Cl}_3} + \underset{\text{Disulphur dichloride.}}{3'\mathbf{S}'_2\mathrm{Cl}_2}.$$

The product must be purified by distillation.

2. It may also be prepared by dissolving antimonious sulphide in hydrochloric acid, or antimony in aqua-regia, evaporating, and distilling the product:

$$\underset{\text{Antimonious sulphide.}}{\mathbf{Sb}_2\mathrm{S}''_3} + \underset{\text{Hydrochloric acid.}}{6\mathrm{HCl}} = \underset{\text{Sulphuretted hydrogen.}}{3\mathbf{S}\mathrm{H}_2} + \underset{\text{Antimonious chloride.}}{2\mathbf{Sb}\mathrm{Cl}_3}.$$

$$2\mathrm{Sb} + \underset{\text{Hydrochloric acid.}}{6\mathrm{HCl}} + \underset{\text{Nitric acid.}}{6\mathbf{N}\mathrm{O}_2\mathrm{Ho}} = \underset{\text{Antimonious chloride.}}{2\mathbf{Sb}\mathrm{Cl}_3} + \underset{\text{Water.}}{6\mathbf{O}\mathrm{H}_2} + \underset{\text{Nitric peroxide.}}{3'\mathbf{N}^{\mathrm{iv}}{}_2\mathrm{O}_4}.$$

The receiver must be changed as soon as the distillate begins to solidify, and the product which is collected above this point must be purified by repeated rectification.

3. It may be conveniently obtained by the distillation of a mixture of 1 part of powdered antimony with 3 parts of mercuric chloride, or of 3 parts of antimonious sulphide with 7 parts of mercuric chloride:

$$\underset{}{Sb_4} + \underset{\text{Mercuric chloride.}}{4HgCl_2} = \underset{\text{Antimonious chloride.}}{2SbCl_3} + \underset{\text{Dimercuric diantimonide.}}{'Sb''_2Hg''_2} + \underset{\text{Mercurous chloride.}}{'Hg'_2Cl_2}.$$

$$\underset{\text{Antimonious sulphide.}}{Sb_2S''_3} + \underset{\text{Mercuric chloride.}}{3HgCl_2} = \underset{\text{Antimonious chloride.}}{2SbCl_3} + \underset{\text{Mercuric sulphide.}}{3HgS}.$$

4. Another method consists in distilling together antimonious sulphate and sodic chloride:

$$\underset{\text{Antimonious sulphate.}}{S_3O_6Sbo'''_2} + \underset{\text{Sodic chloride.}}{6NaCl} = \underset{\text{Antimonious chloride.}}{2SbCl_3} + \underset{\text{Sodic sulphate.}}{3SO_2Nao_2}.$$

Properties.—Antimonious chloride is a soft, colorless, laminated crystalline mass. From its consistency and fusibility, it was formerly known as *butter of antimony.* It is deliquescent and powerfully corrosive.

Reaction.—With water it produces *antimonious oxychloride,* which is thus obtained as a white powder:

$$\underset{\text{Antimonious chloride.}}{SbCl_3} + \underset{\text{Water.}}{OH_2} = \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Antimonious oxychloride.}}{SbOCl}.$$

Long-continued action of water transforms this compound into antimonious oxide:

$$\underset{\text{Antimonious oxychloride.}}{2SbOCl} + \underset{\text{Water.}}{OH_2} = \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Antimonious oxide.}}{Sb_2O_3}.$$

ANTIMONIC CHLORIDE.

$SbCl_5$.

Molecular weight = 297.5. *Fuses at* 0° C.

Preparation.—It is obtained by acting upon antimony with excess of chlorine, or by passing this gas over antimonious chloride, when the latter liquefies, producing antimonic chloride:

$$2Sb + 5Cl_2 = 2\mathbf{Sb}Cl_5.$$

		Antimonic chloride.

$$\mathbf{Sb}Cl_3 + Cl_2 = \mathbf{Sb}Cl_5.$$

Antimonious chloride.		Antimonic chloride.

Properties.—Antimonic chloride is a colorless, fuming liquid. It is readily decomposed on heating into antimonious chloride and free chlorine, and thus behaves towards many substances as a chlorinating agent.

Reactions.—1. With a small quantity of water, it forms antimonic oxytrichloride, analogous to phosphoric oxytrichloride:

$$\mathbf{Sb}Cl_5 + \mathbf{O}H_2 = \mathbf{Sb}OCl_3 + 2HCl.$$

Antimonic chloride.	Water.	Antimonic oxytrichloride.	Hydrochloric acid.

2. An excess of water transforms antimonic chloride into orthantimonic acid, or pyrantimonic acid corresponding to pyrophosphoric acid:

$$\mathbf{Sb}Cl_5 + 4\mathbf{O}H_2 = \mathbf{Sb}OHo_3 + 5HCl,$$

Antimonic chloride.	Water.	Orthantimonic acid.	Hydrochloric acid.

$$\text{or} \quad 2\mathbf{Sb}Cl_5 + 7\mathbf{O}H_2 = \mathbf{Sb}_2O_3Ho_4 + 10HCl.$$

Antimonic chloride.	Water.	Pyrantimonic acid.	Hydrochloric acid.

3. By the action of sulphuretted hydrogen, antimonic sulphotrichloride is formed:

$$\mathbf{Sb}Cl_5 + \mathbf{S}H_2 = \mathbf{Sb}S''Cl_3 + 2HCl.$$

Antimonic chloride.	Sulphuretted hydrogen.	Antimonic sulphotrichloride.	Hydrochloric acid.

Antimonious bromide, $\mathbf{Sb}Br_3$, resembles antimonious chloride. It crystallizes from carbonic disulphide in colorless octahedra. It fuses at 90° C. (194° F.), boils at 275° C. (527° F.), and by the action of water is converted into the *oxybromide*, $\mathbf{Sb}OBr$.

Antimonious iodide, $\mathbf{Sb}I_3$, crystallizes in red hexagonal plates, and, when acted upon by water, forms the *oxyiodide*, $\mathbf{Sb}OI$.

Antimonious fluoride, $\mathbf{Sb}F_3$, is obtained by evaporating a solution of antimonious oxide in excess of hydrofluoric acid. It crystallizes in colorless prisms or scales, and deliquesces with formation of the *oxyfluoride*, $\mathbf{Sb}OF$.

Antimonic fluoride, $\mathbf{Sb}F_5$, is left behind as a gummy mass when a solution of antimonic acid in hydrofluoric acid is evaporated *in vacuo*.

OXIDES AND ACIDS OF ANTIMONY.

Antimonious oxide or anhydride, ...	$(\mathbf{Sb}_2O_3)_2$.
Diantimonic tetroxide, ...	$'\mathbf{Sb}^{iv}{}_2O_4$.
Antimonic anhydride, ...	$\mathbf{Sb}_2O_5$.
Metantimonious acid, ...	$\mathbf{Sb}OHo$.
Orthantimonic acid, ...	$\mathbf{Sb}OHo_3$?
Metantimonic acid, ...	$\mathbf{Sb}O_2Ho$.
Pyrantimonic acid, ...	$\mathbf{Sb}_2O_3Ho_4$.

ANTIMONIOUS OXIDE, or ANHYDRIDE.

$$(\mathbf{Sb}_2O_3)_2.$$

Molecular weight = 576. *Molecular volume* $\square\square$. 1 *litre of antimonious oxide vapor weighs* 288 *criths. Sp. gr.* (*octahedral*) 5.25, (*rhombic*) 5.55.

Occurrence.—Antimonious oxide is found in nature in two rare minerals: in the rhombic form as *valentinite*, and in the octahedral form as *senarmontite.*

Preparation.—1. It is formed when antimony is burnt in air or oxygen.

2. It is most readily obtained by pouring a solution of antimonious chloride in dilute hydrochloric acid into a boiling solution of sodic carbonate:

$2\mathbf{Sb}Cl_3$	+	$3\mathbf{C}ONao_2$	=	$\mathbf{Sb}_2O_3$	+	$3\mathbf{C}O_2$	+	$6NaCl.$
Antimonious chloride.		Sodic carbonate.		Antimonious oxide.		Carbonic anhydride.		Sodic chloride.

3. When metantimonious acid is heated to 100° C., it is converted into antimonious anhydride, with elimination of the elements of water:

$2\mathbf{Sb}OHo$	=	$\mathbf{O}H_2$	+	$\mathbf{Sb}_2O_3.$
Metantimonious acid.		Water.		Antimonious oxide.

Properties.—Antimonious anhydride may be obtained in two distinct crystalline forms—in rhombic prisms and in regular octahedra—corresponding with the two forms of arsenious anhydride, with which substance it is therefore *isodimorphous.* When antimony is heated in a slow current of air, rhombic prisms of the oxide are formed in the immediate neighborhood of the metal; further on a mixture of prisms and octahedra is deposited; whilst in the colder parts of the tube the crystals consist of octahedra alone. Antimonious oxide in both its forms is colorless, but when heated, assumes a yellow tint, which disappears again on cooling. When air is excluded, it may be fused and sublimed. Water does not dissolve it.

Reactions.—1. When heated to redness in air, it burns like tinder, forming diantimonic tetroxide:

$\mathbf{Sb}_2O_3$	+	O	=	$'\mathbf{Sb}^{iv}{}_2O_4.$
Antimonious oxide.				Diantimonic tetroxide.

2. It is really reduced to the metallic state by ignition with charcoal or hydrogen:

Sb_2O_3	+	$3C$	=	$2Sb$	+	$3CO.$
Antimonious oxide.						Carbonic oxide.

Sb_2O_3	+	$3H_2$	=	$2Sb$	+	$3OH_2.$
Antimonious oxide.						Water.

3. It is readily dissolved by a hot solution of hydric potassic tartrate (cream of tartar), forming potassic antimonylic tartrate (tartar emetic):

$$2\left\{\begin{matrix}COHo\\CHHo\\CHHo\\COKo\end{matrix}\right. + Sb_2O_3 = 2\left\{\begin{matrix}CO(Sb'''O_2)\\CHHo\\CHHo\\COKo\end{matrix}\right. + OH_2.$$

Hydric potassic tartrate (cream of tartar),	Antimonious oxide.	Potassic antimonylic tartrate (tartar emetic).	Water.

4. Hydrochloric acid dissolves it with formation of antimonious chloride:

Sb_2O_3	+	$6HCl$	=	$2SbCl_3$	+	$3OH_2.$
Antimonious oxide.		Hydrochloric acid.		Antimonious chloride.		Water.

METANTIMONIOUS ACID.

$SbOHo.$

Molecular weight = 153.

Preparation.—Metantimonious acid is obtained by pouring a solution of antimonious chloride into a cold solution of sodic carbonate:

$2SbCl_3$	+	$3CONao_2$	+	OH_2	=	$2SbOHo$	+	$3CO_2$	+	$6NaCl.$
Antimonious chloride.		Sodic carbonate.		Water.		Metantimonious acid.		Carbonic anhydride.		Sodic chloride.

Properties.—It forms a white amorphous powder, which is insoluble in water.

Reactions.—1. It is decomposed by heat (p. 384).

2. It is dissolved by an excess of alkaline hydrates, producing ill-defined antimonites.

It also possesses weak basic properties and forms salts in which the monad group (SbO) replaces the hydrogen of the acid. Potassic antimonylic tartrate is an example.

DIANTIMONIC TETROXIDE, *Antimonylic Antimonate.*

$$\left\{\begin{matrix}SbO_2\\SbO_2\end{matrix}\right. = {}'Sb^{iv}{}_2O_4,\text{ or } Sb^{v}O_2(Sb'''O_2).$$

Molecular weight = 304.

Occurrence.—Diantimonic tetroxide is found native as *cervantite.*

Preparation.—1. It is obtained by igniting antimonic anhydride, or the white solid produced by the action of nitric acid upon metallic antimony:

$$\underset{\text{Antimonic anhydride.}}{2\mathbf{Sb}_2O_5} = \underset{\text{Diantimonic tetroxide.}}{2'\mathbf{Sb}^{iv}{}_2O_4} + O_2.$$

2. When antimonious oxide is heated in contact with air, it is converted into diantimonic tetroxide (p. 384).

Properties.—Diantimonic tetroxide is a white, infusible and non-volatile powder. When heated, it turns yellow, but becomes white again on cooling.

Reaction.—When boiled with a solution of hydric potassic tartrate, it is decomposed, potassic antimonylic tartrate and metantimonic acid being formed:

$$\underset{\text{Hydric potassic tartrate.}}{\begin{cases} \mathbf{C}OHo \\ \mathbf{C}HHo \\ \mathbf{C}HHo \\ \mathbf{C}OKo \end{cases}} + \underset{\text{Antimonylic antimonate.}}{\mathbf{Sb}^vO_2(Sb'''O_2)} = \underset{\text{Potassic antimonylic tartrate.}}{\begin{cases} \mathbf{C}O(Sb'''O_2) \\ \mathbf{C}HHo \\ \mathbf{C}HHo \\ \mathbf{C}OKo \end{cases}} + \underset{\text{Metantimonic acid.}}{\mathbf{Sb}O_2Ho.}$$

This reaction seems to indicate that this oxide is in reality an antimonylic antimonate as formulated in the above equation.

ANTIMONIC ANHYDRIDE.

$$\mathbf{Sb}_2O_5.$$

Molecular weight = 320. *Sp. gr.* 6.6.

Preparation.—It is obtained by heating the corresponding acids to 280° C. (536° F.):

$$\underset{\text{Orthantimonic acid.}}{2\mathbf{Sb}OHo_3} = \underset{\text{Antimonic anhydride.}}{\mathbf{Sb}_2O_5} + \underset{\text{Water.}}{3\mathbf{O}H_2.}$$

$$\underset{\text{Metantimonic acid.}}{2\mathbf{Sb}O_2Ho} = \underset{\text{Antimonic anhydride.}}{\mathbf{Sb}_2O_5} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

$$\underset{\text{Pyrantimonic acid.}}{\mathbf{Sb}_2O_3Ho_4} = \underset{\text{Antimonic anhydride.}}{\mathbf{Sb}_2O_5} + \underset{\text{Water.}}{2\mathbf{O}H_2.}$$

Properties.—Antimonic anhydride is a pale yellow amorphous substance, insoluble in water.

Reactions.—1. When heated it is decomposed into antimonylic antimonate and oxygen (*supra*). This decomposition begins at 300° C.

2. Fused with potassic carbonate, it produces potassic metantimonate:

$$\underset{\text{Antimonic anhydride.}}{\mathbf{Sb}_2O_5} + \underset{\text{Potassic carbonate.}}{\mathbf{C}OKo_2} = \underset{\text{Potassic metantimonate.}}{2\mathbf{Sb}O_2Ko} + \underset{\text{Carbonic anhydride.}}{\mathbf{C}O_2.}$$

ORTHANTIMONIC ACID.

$\mathbf{Sb}OHo_3$?

Preparation.—This acid is said to be formed by the action of water upon antimonic chloride (p. 383).

METANTIMONIC ACID.

$\mathbf{Sb}O_2Ho.$

Preparation.—1. It is obtained by the action of nitric acid containing a little hydrochloric acid on metallic antimony:

$$\underset{}{Sb_2} + \underset{\text{Nitric acid.}}{4\mathbf{N}O_2Ho} = \underset{\text{Metantimonic acid.}}{2\mathbf{Sb}O_2Ho} + \underset{\text{Nitrous anhydride.}}{\mathbf{N}_2O_3} + \underset{\text{Nitric oxide.}}{'\mathbf{N}''_2O_2} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

2. It is also formed by the spontaneous dehydration of orthantimonic acid, or of pyrantimonic acid:

$$\underset{\text{Orthantimonic acid.}}{\mathbf{Sb}OHo_3} = \underset{\text{Water.}}{\mathbf{O}H_2} + \underset{\text{Metantimonic acid.}}{\mathbf{Sb}O_2Ho.}$$

$$\underset{\text{Pyrantimonic acid.}}{\mathbf{Sb}_2O_3Ho_4} = \underset{\text{Water.}}{\mathbf{O}H_2} + \underset{\text{Metantimonic acid.}}{2\mathbf{Sb}O_2Ho.}$$

Properties.—It is a soft white powder, sparingly soluble in water. The solution reddens litmus.

Reaction.—By the action of alkaline hydrates, it produces either metantimonates or orthantimonates:

$$\underset{\text{Metantimonic acid.}}{\mathbf{Sb}O_2Ho} + \underset{\text{Potassic hydrate.}}{\mathbf{O}KH} = \underset{\text{Potassic metantimonate.}}{\mathbf{Sb}O_2Ko} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

$$\underset{\text{Metantimonic acid.}}{\mathbf{Sb}O_2Ho} + \underset{\text{Potassic hydrate.}}{\mathbf{O}KH} = \underset{\text{Dihydric potassic orthantimonate.}}{\mathbf{Sb}OHo_2Ko.}$$

PYRANTIMONIC ACID, *Parantimonic Acid* (*Metantimonic Acid of Fremy*).

$\mathbf{Sb}_2O_3Ho_4.$

Preparation.—1. It is formed by the action of water upon antimonic chloride (p. 383).

2. It is also obtained by acidifying solutions of pyrantimonates:

$$\underset{\text{Dihydric dipotassic pyrantimonate.}}{\mathbf{Sb}_2O_3Ho_2Ko_2} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Pyrantimonic acid.}}{\mathbf{Sb}_2O_3Ho_4} + \underset{\text{Potassic chloride.}}{2KCl.}$$

Dihydric dipotassic pyrantimonate is prepared by fusing antimonic anhydride with an excess of potassic hydrate, and extracting the mass with water, when an alkaline solution containing dihydric dipotassic pyrantimonate, $\mathbf{Sb}_2O_3Ho_2Ko_2$, is obtained. This solution produces precipitates in solutions of sodium salts, the sodic pyrantimonate thus formed having the formula $\mathbf{Sb}_2O_3Ho_2Nao_2,6\mathbf{O}H_2$.

COMPOUNDS OF ANTIMONY WITH SULPHUR.

Antimonious sulphide, ...	$\mathbf{Sb}_2S''_3$.
Antimonic sulphide, ...	$\mathbf{Sb}_2S''_5$.

ANTIMONIOUS SULPHIDE, *Sulphantimonious Anhydride.*

$$Sb_2S''_3.$$

Molecular weight = 336.

Occurrence.—Antimonious sulphide is found in nature as *stibnite* or *gray antimony ore.*

Preparation.—1. It may be obtained by heating together antimony and sulphur, or antimonious oxide and sulphur, in the proper molecular proportions:

$$Sb_4 + 3S_2 = \underset{\substack{\text{Antimonious}\\\text{sulphide.}}}{2Sb_2S''_3}.$$

$$\underset{\substack{\text{Antimonious}\\\text{oxide.}}}{2Sb_2O_3} + 9S = \underset{\substack{\text{Antimonious}\\\text{sulphide.}}}{2Sb_2S''_3} + \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{3SO_2}.$$

2. It is precipitated when sulphuretted hydrogen is passed through a solution of antimonious chloride:

$$\underset{\substack{\text{Antimonious}\\\text{chloride.}}}{2SbCl_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3SH_2} = \underset{\substack{\text{Antimonious}\\\text{sulphide.}}}{Sb_2S''_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl}.$$

Properties.—The native sulphide occurs in dark-gray radiating crystalline masses, with a metallic lustre—less frequently in rhombic prisms. The precipitated substance is an orange-red amorphous powder, containing water of hydration which may be expelled by heating. Antimonious sulphide is readily fusible, and may be sublimed.

Reactions.—1. Hot hydrochloric acid decomposes it, forming antimonious chloride and sulphuretted hydrogen (see p. 381).

2. It dissolves with decomposition in solutions of alkaline hydrates, yielding a mixture of antimonite and sulphantimonite:

$$\underset{\substack{\text{Antimonious}\\\text{sulphide.}}}{Sb_2S''_3} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{6KHo} = \underset{\substack{\text{Trisulphopotassic}\\\text{sulphantimonite.}}}{SbKs_3} + \underset{\substack{\text{Tripotassic}\\\text{antimonite.}}}{SbKo_3} + \underset{\text{Water.}}{3OH_2}.$$

The addition of an acid reproduces and precipitates the antimonious sulphide:

$$\underset{\substack{\text{Trisulphopotassic}\\\text{sulphantimonite.}}}{SbKs_3} + \underset{\substack{\text{Tripotassic}\\\text{antimonite.}}}{SbKo_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Antimonious}\\\text{sulphide.}}}{Sb_2S''_3}$$

$$+ \underset{\text{Potassic chloride.}}{6KCl} + \underset{\text{Water.}}{3OH_2}.$$

3. It dissolves in a solution of an alkaline sulphhydrate, forming a sulphantimonite:

$$\underset{\substack{\text{Antimonious}\\\text{sulphide.}}}{Sb_2S''_3} + \underset{\substack{\text{Potassic}\\\text{sulphhydrate.}}}{6KHs} = \underset{\substack{\text{Trisulphopotassic}\\\text{sulphantimonite.}}}{2SbKs_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3SH_2}.$$

SULPHANTIMONITES.

Many sulphantimonites occur in nature:

Orthosulphantimonites.

General formulæ: $\mathbf{Sb}Ms_3$ and $\mathbf{Sb}_2Ms''_3$.

Dark-red silver. *Trisulphargentic sulphantimonite,* . $\mathbf{Sb}Ags_3$.
Boulangerite. *Trisulphoplumbic sulphantimonite,* . . $\mathbf{Sb}_2Pbs''_3$.
Bournonite. *Disulphoplumbic sulphocuprous sulphantimonite,* . . . . $\mathbf{Sb}_2Pbs''_2(Cu_2S''_2)''$.

Metasulphantimonites.

General formulæ: $\mathbf{Sb}S''Ms$ and $\mathbf{Sb}_2S''_2Ms''$.

Miargyrite. *Sulphargentic metasulphantimonite,* . . $\mathbf{Sb}S''Ags$.
Zinkenite. *Sulphoplumbic metasulphantimonite,* . . $\mathbf{Sb}_2S''_2Pbs''$.
Antimony copper glance. *Sulphocuprous metasulphantimonite,* . . . . $\mathbf{Sb}_2S''_2(Cu_2S''_2)''$.
Berthierite. *Sulphoferrous metasulphantimonite,* . . $\mathbf{Sb}_2S''_2Fes''$.

Pyrosulphantimonites.

General formulæ: $\mathbf{Sb}_2S''Ms_4$ and $\mathbf{Sb}_2S''Ms''_2$.

Feather ore. *Sulphoplumbic pyrosulphantimonite,* . . $\mathbf{Sb}_2S''Pbs''_2$.
Fahl ore. *Sulphocuprosoferrous pyrosulphantimonite,* . $\mathbf{Sb}_2S''(Cu_2FeS''_2)''$.

A soluble *colloidal modification* of antimonious sulphide corresponding with colloidal arsenious sulphide (p. 375) is also known.

ANTIMONIC SULPHIDE, *Sulphantimonic Anhydride.*

$$\mathbf{Sb}_2S''_5.$$

Molecular weight = 400.

Preparation.—1. It is precipitated as a yellowish-red powder when sulphuretted hydrogen is passed through a solution of antimonic chloride:

$$\underset{\text{Antimonic chloride.}}{2\mathbf{Sb}Cl_5} + \underset{\text{Sulphuretted hydrogen.}}{5\mathbf{S}H_2} = \underset{\text{Antimonic sulphide.}}{\mathbf{Sb}_2S''_5} + \underset{\text{Hydrochloric acid.}}{10HCl.}$$

2. The same precipitate is formed by the addition of an acid to a solution of a sulphantimonate:

$$\underset{\text{Trisulphosodic sulphantimonate.}}{2\mathbf{Sb}S''Nas_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Antimonic sulphide.}}{\mathbf{Sb}_2S''_5} + \underset{\text{Sodic chloride.}}{6NaCl} + \underset{\text{Sulphuretted hydrogen.}}{3\mathbf{S}H_2.}$$

Reactions.—1. When heated it is decomposed into antimonious sulphide and free sulphur.

2. Boiling hydrochloric acid decomposes it into antimonious chloride, sulphuretted hydrogen, and sulphur:

$$Sb_2S''_5 + 6HCl = 2SbCl_3 + 3SH_2 + S_2.$$

Antimonic sulphide.	Hydrochloric acid.	Antimonious chloride.	Sulphuretted hydrogen.

3. It dissolves in a solution of an alkaline sulphide, forming a sulphantimonate:

$$Sb_2S''_5 + 3SK_2 = 2SbS''Ks_3.$$

Antimonic sulphide.	Potassic sulphide.	Trisulphopotassic sulphantimonate.

4. It is soluble in a solution of an alkaline hydrate, a mixture of antimonate and sulphantimonate being formed:

$$4Sb_2S''_5 + 24OKH = 3SbOKo_3 + 5SbS''Ks_3 + 12OH_2.$$

Antimonic sulphide.	Potassic hydrate.	Tripotassic antimonate.	Trisulphopotassic sulphantimonate.	Water.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF ANTIMONY:

Antimonious Compounds.—Solutions of antimonious oxide in acids became milky on dilution with water. The milkiness disappears on addition of tartaric acid. (Distinction from bismuth compounds.) *Sulphuretted hydrogen* precipitates from acid solutions orange-colored antimonious sulphide, soluble in concentrated hydrochloric acid, in caustic alkalies, and in ammonic sulphide, almost insoluble in ammonic carbonate, insoluble in hydric potassic sulphite. If a hydrochloric acid solution of the sulphide or of any other compound of antimony be brought into a platinum dish along with a piece of zinc, the antimony is deposited by voltaic action as a black coating adhering to the platinum, whilst any tin which may be present is precipitated as a gray powder on the zinc. The hydrochloric acid solution of an antimonious compound precipitates gold in the metallic form from its solutions.

Antimonic Compounds.—These yield in acid solution with *sulphuretted hydrogen* a yellowish-red precipitate of antimonic sulphide which is soluble in the same reagents as the antimonious compound.

The compounds of antimony when introdueed into Marsh's apparatus (p. 377) evolve antimoniuretted hydrogen. The flame of this gas deposits, upon a cold surface of porcelain, a stain of metallic antimony, which is blacker and less lustrous than that of arsenic. A mirror of metallic antimony is also formed when the gas is passed through a heated tube. These coatings may be distinguished from those of arsenic by their almost total insolubility in sodic hypochlorite. When heated with potassic cyanide upon charcoal in the reducing flame of the blowpipe, compounds of antimony yield a brittle metallic regulus, and the charcoal becomes covered with a white incrustation; but no odor of garlic is perceptible as in the case of arsenic.

BISMUTH, Bi_4?

Atomic weight = 208.2. *Sp. gr.* 9.83. *Fuses at* 265° C. *Atomicity* $'''$ *and* ^{v}. *Evidence of atomicity:*

Bismuthous chloride,	$\mathbf{Bi}'''Cl_3$.
Bismuthous oxide,	$\mathbf{Bi}'''_2O_3$.
Bismuthous ethide,	$\mathbf{Bi}'''Et_3$.
Bismuthous dichlorethide,	$\mathbf{Bi}'''EtCl_2$.
Bismuthic anhydride,	$\mathbf{Bi}^{v}_2O_5$.
Metabismuthic acid,	$\mathbf{Bi}^{v}O_2Ho$.

Occurrence.—Bismuth is found principally in the metallic state, but it also occurs in combination with oxygen, sulphur, and tellurium.

Preparation.—1. The method of extraction from the ores formerly consisted in heating the crude native bismuth in sloping iron tubes placed in a furnace. The metal fused and ran off, whilst the impurities were left in the tubes. The bismuth thus obtained was contaminated with sulphur, arsenic, iron, and other metals.

2. At the present day large quantities of bismuth are obtained as a by-product in the manufacture of smalt (*q.v.*). The crude bismuth is purified by fusing at the lowest possible temperature, when the more fusible bismuth runs off, leaving the iron, nickel, and other impurities behind.

3. It may be obtained in the pure state by dissolving commercial bismuth in nitric acid, precipitating the basic nitrate by the addition of water, and reducing the precipitate by ignition with charcoal.

Properties.—Bismuth is a grayish-white metal with a slight reddish tinge. It crystallizes in rhombohedra which approximate closely to the cube. At a very high temperature it volatilizes. It is not oxidized by exposure to the air at ordinary temperatures, but, when strongly heated, burns, forming bismuthous oxide.

Uses.—Metallic bismuth is employed in the preparation of fusible alloys, such as *Rose's metal* and *Wood's metal* (*q.v.*).

No compound of bismuth with hydrogen is known.

HALOGEN AND OXYHALOGEN COMPOUNDS OF BISMUTH.

BISMUTHOUS CHLORIDE.

$\mathbf{BiCl_3}$.

Molecular weight = 314.7. *Molecular volume* □□. 1 *litre of bismuthous chloride vapor weighs* 157.35 *criths.*

Preparation.—1. It is formed when dry chlorine is passed over metallic bismuth:

$$\underset{}{Bi_2} + 3Cl_2 = \underset{\text{Bismuthous chloride.}}{2BiCl_3.}$$

2. It may be obtained by evaporating a solution of bismuth in hydrochloric acid containing a little nitric acid, and distilling the residue.

3. Another method consists in distilling bismuth with mercuric chloride:

$$Bi_2 + \underset{\text{Mercuric chloride.}}{6HgCl_2} = \underset{\text{Bismuthous chloride.}}{2BiCl_3} + \underset{\text{Mercurous chloride.}}{3'Hg'_2Cl_2.}$$

Properties.—It forms a white fusible deliquescent mass which may be distilled.

Reaction.—Water decomposes it, precipitating *bismuthous oxychloride* as a white powder:

$$\underset{\text{Bismuthous chloride.}}{BiCl_3} + \underset{\text{Water.}}{OH_2} = \underset{\text{Bismuthous oxychloride.}}{BiOCl} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

Dibismuthous tetrachloride, $\left\{\begin{matrix} BiCl_2 \\ BiCl_2 \end{matrix}\right.$, is obtained as a black amorphous mass by heating bismuthous chloride with bismuth.

Bismuthous bromide, $BiBr_3$, forms yellow prisms fusing at 200° C. Water converts it into *bismuthous oxybromide*, $BiOBr$.

Bismuthous iodide, BiI_3, is obtained by heating a mixture of bismuth and iodine. It sublimes in lustrous, dark-gray hexagonal plates. By boiling with water it is decomposed into hydriodic acid and copper-colored *bismuthous oxyiodide*, $BiOI$.

Bismuthous fluoride, BiF_3, is obtained as a white powder by evaporating a solution of bismuthous oxide with an excess of hydrofluoric acid:

$$\underset{\text{Bismuthous oxide.}}{Bi_2O_3} + \underset{\text{Hydrofluoric acid.}}{6HF} = \underset{\text{Bismuthous fluoride.}}{2BiF_3} + \underset{\text{Water.}}{3OH_2.}$$

COMPOUNDS OF BISMUTH WITH OXYGEN AND HYDROXYL.

Dibismuthous dioxide, ...	$\left\{\begin{matrix} BiO \\ BiO \end{matrix}\right.$
Bismuthous oxide, ...	Bi_2O_3.
Dibismuthic tetroxide, ...	$'Bi^{iv}{}_2O_4$.
Bismuthic anhydride, ...	Bi_2O_5.
Bismuthous oxyhydrate, or metabismuthous acid,	$BiOHo$.
Metabismuthic acid, ...	BiO_2Ho.

DIBISMUTHOUS DIOXIDE.

$$\left\{\begin{matrix} BiO \\ BiO \end{matrix}\right.$$

Molecular weight = 448.4.

Preparation.—When a mixture of stannous and bismuthous chlorides is poured into an excess of dilute caustic potash, a black precipitate of dibismuthous dioxide is formed. The reaction takes place in two stages. In the first, dipotassic stannite and tripotassic bismuthite are formed; these salts then react upon each other:

$$\underset{\substack{\text{Tripotassic}\\\text{bismuthite.}}}{2\mathbf{Bi}Ko_3} + \underset{\substack{\text{Dipotassic}\\\text{stannite.}}}{\mathbf{Sn}Ko_2} + \underset{\text{Water.}}{3\mathbf{O}H_2} = \underset{\substack{\text{Dibismuthous}\\\text{dioxide.}}}{'\mathbf{Bi}''_2O_2} + \underset{\substack{\text{Dipotassic}\\\text{stannate.}}}{\mathbf{Sn}OKo_2} + \underset{\substack{\text{Potassic}\\\text{hydrate.}}}{6\mathbf{O}KH.}$$

The precipitate of dibismuthous dioxide must be filtered and washed out of contact with air and then dried by heating in a current of carbonic anhydride. It is thus obtained as a gray crystalline powder.

Reactions.—1. The moist substance when exposed to the air oxidizes spontaneously to bismuthous oxide:

$$\underset{\substack{\text{Dibismuthous}\\\text{dioxide.}}}{'\mathbf{Bi}''_2O_2} + O = \underset{\substack{\text{Bismuthous}\\\text{oxide.}}}{\mathbf{Bi}_2O_3.}$$

In the same way when the dried compound is heated in the air, it glows like tinder and is converted into bismuthous oxide.

2. Hydrochloric acid decomposes it into bismuthous chloride and bismuth:

$$\underset{\substack{\text{Dibismuthous}\\\text{dioxide.}}}{3'\mathbf{Bi}''_2O_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{12HCl} = \underset{\substack{\text{Bismuthous}\\\text{chloride.}}}{4\mathbf{Bi}Cl_3} + \mathbf{Bi}_2 + \underset{\text{Water.}}{6\mathbf{O}H_2.}$$

BISMUTHOUS OXIDE.

$$\mathbf{Bi}_2O_3.$$

Molecular weight = 464.4. *Sp. gr.* 8.2.

Occurrence.—This substance is found in nature as the rare mineral *bismuth ochre.*

Preparation.—1. It is formed when bismuth is burnt in air or oxygen.

2. It is left behind when the nitrate, carbonate, or hydrate is heated:

$$\underset{\substack{\text{Bismuthous}\\\text{nitrate.}}}{2\mathbf{N}_3O_6Bio'''} = \underset{\substack{\text{Bismuthous}\\\text{oxide.}}}{\mathbf{Bi}_2O_3} + \underset{\substack{\text{Nitrous}\\\text{anhydride.}}}{3\mathbf{N}_2O_3} + 3O_2.$$

$$\underset{\substack{\text{Bismuthous nitrate}\\\text{dihydrate.}}}{2\mathbf{N}O_2(Bi'''Ho_2O)} = \underset{\substack{\text{Bismuthous}\\\text{oxide.}}}{\mathbf{Bi}_2O_3} + \underset{\text{Water.}}{2\mathbf{O}H_2} + \underset{\substack{\text{Nitrous}\\\text{anhydride.}}}{\mathbf{N}_2O_3} + O_2.$$

$$\underset{\substack{\text{Bismuthylic}\\\text{carbonate.}}}{\mathbf{C}O(BiO_2)_2} = \underset{\substack{\text{Bismuthous}\\\text{oxide.}}}{\mathbf{Bi}_2O_3} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{\mathbf{C}O_2.}$$

$$\underset{\substack{\text{Bismuthous}\\\text{oxyhydrate.}}}{2\mathbf{Bi}OHo} = \underset{\substack{\text{Bismuthous}\\\text{oxide.}}}{\mathbf{Bi}_2O_3} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

3. When bismuthous hydrate is dissolved in a solution of potassic hydrate and boiled, it parts with the elements of water, and is precipitated as bismuthous oxide.

Properties.—Bismuthous oxide is a yellow insoluble powder, which becomes darker on heating, and then fuses. The oxide obtained by boiling the solution of the hydrate in caustic alkali is crystalline.

Reaction.—It is dissolved by hydrochloric, nitric, and sulphuric acids, forming the bismuthous chloride, nitrate, and sulphate:

$\mathbf{BiCl_3}$.	$\mathbf{N_3O_6Bio'''}$.	$\mathbf{S_3O_6Bio'''_2}$.
Bismuthous chloride.	Bismuthous nitrate.	Bismuthous sulphate.

Salts of Bismuthous Oxide.—These salts are soluble only in water containing an excess of acid. Pure water decomposes them into basic salts and free acid:

$$\underset{\text{Bismuthous nitrate.}}{N_3O_6Bio'''} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Bismuthous nitrate dihydrate.}}{NO_2(Bi'''Ho_2O)} + \underset{\text{Nitric acid.}}{2NO_2Ho}.$$

BISMUTHOUS OXYHYDRATE, *Metabismuthous Acid.*

BiOHo.

Preparation.—By pouring a solution of bismuthous nitrate in dilute nitric acid into dilute ammonia or potassic hydrate, a precipitate is formed, which probably contains orthobismuthous acid. On drying this precipitate at 100° C., metabismuthous acid is obtained as a white amorphous mass:

$$\underset{\text{Bismuthous nitrate.}}{N_3O_6Bio'''} + \underset{\text{Potassic hydrate.}}{3OKH} = \underset{\text{Orthobismuthous acid.}}{BiHo_3} + \underset{\text{Potassic nitrate.}}{3NO_2Ko}.$$

$$\underset{\text{Orthobismuthous acid.}}{BiHo_3} = \underset{\text{Metabismuthous acid.}}{BiOHo} + \underset{\text{Water.}}{OH_2}.$$

Reaction.—By heat or by boiling with caustic alkali, water is expelled and bismuthous oxide is formed (see p. 393).

An unstable metabismuthite is produced by fusing bismuthous oxide with sodic carbonate:

$$\underset{\text{Bismuthous oxide.}}{Bi_2O_3} + \underset{\text{Sodic carbonate.}}{CONao_2} = \underset{\text{Sodic metabismuthite.}}{2BiONao} + \underset{\text{Carbonic anhydride.}}{CO_2}.$$

BISMUTHIC ANHYDRIDE.

Bi_2O_5.

Preparation.—This compound is obtained as a brown powder by heating bismuthic acid to 130° C.

Reactions.—1. When heated to the boiling point of mercury it loses oxygen, being converted either into bismuthous oxide or into dibismuthic tetroxide:

$$\underset{\text{Bismuthic anhydride.}}{\mathbf{Bi}_2O_5} = \underset{\text{Bismuthous oxide.}}{\mathbf{Bi}_2O_3} + O_2;$$

$$\underset{\text{Bismuthic andydride.}}{2\mathbf{Bi}_2O_5} = \underset{\text{Dibismuthic tetroxide.}}{2'\mathbf{Bi}^{\text{iv}}{}_2O_4} + O_2.$$

2. When heated in a current of hydrogen, it is readily reduced to bismuthous oxide.

3. Heated with hydrochloric acid it evolves chlorine, producing bismuthous chloride and water:

$$\underset{\text{Bismuthic anhydride.}}{\mathbf{Bi}_2O_5} + \underset{\text{Hydrochloric acid.}}{10HCl} = \underset{\text{Bismuthous chloride.}}{2\mathbf{Bi}Cl_3} + \underset{\text{Water.}}{5\mathbf{O}H_2} + 2Cl_2.$$

4. Sulphurous acid converts it into bismuthous sulphate:

$$\underset{\text{Bismuthic anhydride.}}{3\mathbf{Bi}_2O_5} + \underset{\text{Sulphurous acid.}}{6\mathbf{S}OHo_2} = \underset{\text{Bismuthous sulphate.}}{2\mathbf{S}_3O_6Bio'''_2} + \underset{\text{Bismuthous oxide.}}{\mathbf{Bi}_2O_3} + \underset{\text{Water.}}{6\mathbf{O}H_2}.$$

5. When heated with sulphuric or nitric acid it evolves oxygen, producing bismuthous sulphate or nitrate:

$$\underset{\text{Bismuthic anhydride.}}{\mathbf{Bi}_2O_5} + \underset{\text{Sulphuric acid.}}{3\mathbf{S}O_2Ho_2} = \underset{\text{Bismuthous sulphate.}}{\mathbf{S}_3O_6Bio'''_2} + \underset{\text{Water.}}{3\mathbf{O}H_2} + O_2;$$

$$\underset{\text{Bismuthic anhydride.}}{\mathbf{Bi}_2O_5} + \underset{\text{Nitric acid.}}{6\mathbf{N}O_2Ho} = \underset{\text{Bismuthous nitrate.}}{2\mathbf{N}_3O_6Bio'''} + \underset{\text{Water.}}{3\mathbf{O}H_2} + O_2.$$

METABISMUTHIC ACID.

$$\mathbf{Bi}O_2Ho.$$

Preparation.—Metabismuthic acid is obtained as a red deposit by passing chlorine through a solution of potassic hydrate containing bismuthous oxide in suspension:

$$\underset{\text{Potassic hydrate.}}{4\mathbf{O}KH} + 2Cl_2 + \underset{\text{Bismuthous oxide.}}{\mathbf{Bi}_2O_3} = \underset{\text{Metabismuthic acid.}}{2\mathbf{Bi}O_2Ho} + \underset{\text{Potassic chloride.}}{4KCl} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

Reaction.—It dissolves in a hot solution of potassic hydrate. By the addition of an acid to the liquid a salt, said to have the composition

$$\mathbf{Bi}_2O_4HoKo,$$

is precipitated.

COMPOUNDS OF BISMUTH WITH SULPHUR.

Dibismuthous disulphide, ... $'\mathbf{Bi}''_2S''_2$.
Bismuthous sulphide, ... $\mathbf{Bi}_2S''_3$.

DIBISMUTHOUS DISULPHIDE.

$$\left\{\begin{matrix}\mathbf{Bi}S'' \\ \mathbf{Bi}S''\end{matrix}\right., \text{ or } '\mathbf{Bi}''_2S''_2.$$

Sp. gr. 7.3.

Preparation.—Dibismuthous disulphide is obtained as a mass of gray, metallic acicular crystals by fusing together bismuth and sulphur in the proper molecular proportions.

BISMUTHOUS SULPHIDE.

$\mathbf{Bi}_2S''_3$.

Sp. gr. 6.4.

Occurrence.—Bismuthous sulphide is found native as the rare mineral *bismuth glance.* It forms rhombic crystals and foliated or fibrous masses with a metallic lustre.

Preparation.—1. It may be obtained by fusing together bismuth and sulphur in the proper molecular proportions.

2. It is also obtained as a blackish-brown powder by precipitating bismuth solutions by sulphuretted hydrogen:

$2\mathbf{Bi}Cl_3$	$+$	$3SH_2$	$=$	$\mathbf{Bi}_2S''_3$	$+$	$6HCl$.
Bismuthous chloride.		Sulphuretted hydrogen.		Bismuthous sulphide.		Hydrochloric acid.

Reaction.—This compound is not dissolved by alkaline hydrates or sulphydrates.

A few sulphobismuthites are found in nature:

Kobellite. *Trisulphoplumbic sulphobismuthite*	$\mathbf{Bi}_2Pbs''_3$.
Needle ore. *Disulphoplumbic-dicuprous sulphobismuthite*	$\mathbf{Bi}_2Pbs''_2('Cu'_2S_2)''$.

Bismuthous telluride, $\mathbf{Bi}_2Te''_3$, occurs native as *telluric bismuth* or *tetradymite.* It forms gray, metallic, rhombohedral crystals or foliated masses. A portion of the tellurium in this mineral is generally replaced by sulphur.

General Properties and Reactions of the Compounds of Bismuth.—The salts of bismuth with colorless acids are colorless. Their solutions have an acid reaction. Dilution with water causes the solutions to become milky, owing to the separation of a basic salt. Mineral acids redissolve this basic salt; but the presence of tartaric acid does not prevent or remove the milkiness as in the case of antimony. *Caustic alkalies* and *ammonia* precipitate white bismuthous hydrate, insoluble in excess. *Sulphuretted hydrogen* gives a brown precipitate of bismuthous sulphide, insoluble in ammonic sulphide and in caustic alkalies, soluble in hot nitric acid. *Potassic chromate* precipitates yellow bismuthous chromate, soluble in nitric acid, insoluble in caustic alkalies. (Distinction from plumbic chromate.) Heated on charcoal in the reducing flame the bismuth compounds yield a brittle metallic bead, whilst the charcoal becomes covered with a yellow incrustation.

THE METALS.

CHAPTER XXXI.

DISTINGUISHING CHARACTERISTICS OF THE METALLIC ELEMENTS.

THERE are certain broad differences which prevail between metallic and non-metallic elements, so that as a rule members of the one class may be readily distinguished from those of the other. The most obvious of these differences are physical.

Thus the power of reflecting light is much more marked in the metals than in the non-metals. This power, when intensified by the perfect or almost perfect opacity of the reflecting substance—a property possessed in the highest degree by the metals—constitutes the phenomenon of metallic lustre. The non-metals are generally either transparent or translucent: they admit light into their interior, where it is either transmitted further, or absorbed and dispersed, and they cannot therefore possess the high reflecting power—the power of giving back the whole or nearly the whole of the light which falls upon them—necessary to the production of the metallic lustre. Smoothness of surface is, however, a necessary condition of metallic lustre, and for this reason finely-divided metals do not possess this property. Gold, silver, platinum, and other metals may be obtained in this condition by precipitation from their solutions; but these non-lustrous powders assume a lustre under the burnisher.

Again, the metals are much better conductors of heat and of electricity than the non-metals.

The above broad physical differences have their counterparts in the chemical characters of the elements; thus a metal uniting with oxygen generally yields a base or alkali, whilst the compounds of the non-metals with oxygen generally possess acid properties.

But nature abhors classification, and renders futile all our attempts to form exclusive families of her productions. The animal and vegetable kingdoms merge into each other, so that it is impossible to predicate definitely of the intermediate members to which class they belong—whether they are to be regarded as plants or as animals. In like manner the metals and the non-metals gradually approach and overlap each other in respect of nearly all the so-called distinctive properties just enumerated.

Thus, as regards lustre, we find that various non-metals possess a lustre which is distinctly metallic in character—for example, graphite, the popular name for which, black-*lead*, is derived from this property. Iodine is another instance: the crystals of this substance have a lustre

resembling that of graphite, and not much inferior to that of metallic arsenic when sublimed in a glass tube.

Again, as regards opacity, which was stated to be a general property of the metals, we find that this rule is not absolute. Gold in very thin leaves transmits a green light, silver a blue light, whilst, on the other hand, graphite is opaque, and iodine nearly so.

Again, as regards the power of conducting heat and electricity, carbon in the form of graphite shares this power with the metals.

As to chemical character also, the classification above given does not always hold. Thus some metals yield acids with oxygen—chromic acid, manganic acid, molybdic acid, and others. But no non-metal yields a decided base with oxygen. Tellurium and arsenic yield no base, and the basic properties of antimony and bismuth are very weak.

Although, therefore, the division of the elements into metals and non-metals cannot lay claim to rigid accuracy, it may, in the present state of the science, be regarded as a good practical classification. With the few exceptions just enumerated, it is no more difficult to distinguish a metal from a non-metal than to distinguish an animal from a plant.

Relations of the Metals to Heat.

Expansion by Heat.—Metals as a rule expand more on heating than non-metals. The following table gives the length to which the unit length of a number of substances, measured at 0° C., expands when the substance is heated to 100° C. (212° F.). This value, diminished by unity, is therefore the coefficient of linear expansion for a rise of 100° C.:

Expansion of Solids by Heat.

One part by length measured at 0° C. measures at 100° C.:

English flint glass,	1.000811
French glass tube,	1.000861
Platinum,	1.000844
Palladium,	1.001000
Untempered steel,	1.001079
Antimony,	1.001083
Iron,	1.001182
Bismuth,	1.001392
Gold,	1.001466
Copper,	1.001718
Brass,	1.001866
Silver,	1.001909
Tin (East India),	1.001937
Lead,	1.002848
Zinc,	1.002942

Fusibility.—Another important property of metals is their degree of fusibility. This is almost as varied in the different metals as the range of temperature at our command. On the one hand mercury fuses at —39.5° C. (—39.1° F.), and gallium with the heat of the hand, whilst

iridium scarcely melts in the oxyhydrogen flame, requiring the voltaic arc for its complete liquefaction. Ruthenium is still more infusible, and osmium has never been melted. The following table contains the fusing-points of some of the metals:

Name of metal.	Fusing-point.
Mercury,	—39.5° C. (—39.1° F.).
Gallium,	+30.1 " (+86.2 ").
Potassium,	62.5 " (144.5 ").
Sodium,	95.6 " (204.1 ").
Lithium,	180 " (356 ").
Tin,	228 " (443.4 ").
Bismuth,	268 " (514.4 ").
Thallium,	294 " (561.2 ").
Cadmium,	320 " (608 ").
Lead,	326 " (618.8 ").
Zinc,	420 " (792 ").
Antimony,	430 " (810 ").
Silver,	1040 " (1872 ").

The fusing-point of alloys is always lower than the mean fusing-point of their constituents—taking the relative proportion of the constituents into account in calculating this mean; and sometimes lower than the lowest fusing-point of any of the constituents. Thus Wood's *fusible metal,* which is an alloy of 4 parts of bismuth, 2 of lead, 1 of tin, and 1 of cadmium, fuses at 60.5° C. (140.9° F.). The alloy of potassium and sodium is liquid at ordinary temperatures.

Volatility.—All metals are volatile, but usually only at very high temperatures. Mercury boils at 360° C. (680° F.), but is volatile at ordinary temperatures, as may be shown by suspending a piece of gold-leaf from the stopper of a bottle containing mercury: in course of time, the gold-leaf becomes white, owing to the absorption of the vapor of mercury. Arsenic volatilizes below redness without first assuming the liquid form. Cadmium boils at 860° C. (1580° F.); zinc at 1040° C. (1904° F.). Potassium and sodium are distilled in their manufacture. Lead is volatilized in the process of lead smelting, and means are employed to condense the lead which would thus otherwise escape. Even copper is perceptibly volatile at the temperature of the smelting furnace.

Relations of Metals to Light.

Colors of Solid Metals.—Most metals appear nearly colorless when polished. Some, however, exhibit, even when viewed in the ordinary way, specific colors: thus copper is red; and gold, calcium, and barium display shades of yellow. By causing the light to be reflected several times from their surfaces, some metals, which under ordinary conditions appear colorless, may be made to exhibit color, whilst in the case of the colored metals the particular shade is intensified or altered. Thus by multiple reflection the following metals display the annexed colors:

Copper, ...	scarlet
Gold, ...	red
Silver, ...	pure yellow
Zinc, ...	indigo blue
Iron, ...	violet.

At large angles of incidence—that is, when the light falls very obliquely upon the surface—all metals reflect white light. But their specific reflective power for the different rays varies more as the incident light becomes more perpendicular.

Colors of Ignited Liquid Metals.—At high temperatures, metals in the liquid state generally emit white light; but molten copper gives out a ruddy glow, and molten gold emits a beautiful green light.

Colors of Ignited Vaporous Metals.—All metallic vapors exhibit at very high temperatures characteristic phenomena of color, and some possess, even at relatively low temperatures, colors more or less marked. Thus tin gives a blue vapor; copper a green; silver a green of a different shade; gold a blue; and sodium a yellow. The nature of the colors which metallic and other vapors display at high temperatures forms the subject matter of Spectrum Analysis.

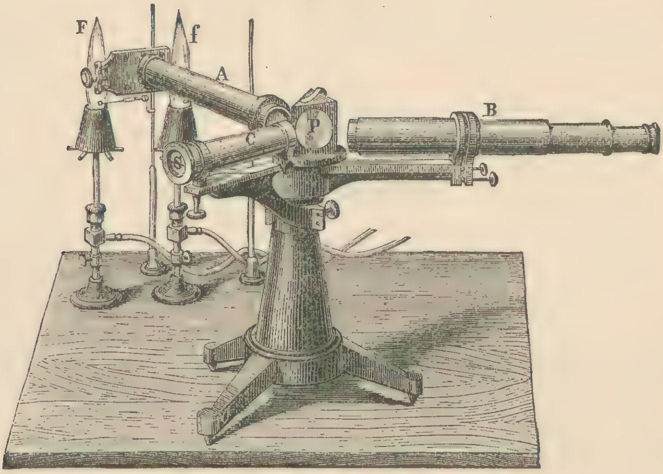
Spectrum Analysis.

The study of the colors of the vaporous elements at high temperatures has developed, in the hands of chemists, into an invaluable method of analysis, surpassing in scope and delicacy all other known methods. This method is known as *spectrum analysis*, and the instrument by means of which the discrimination of the colors of the vapors is effected is the *spectroscope*. Although this method has been employed by chemists only since 1860, it has already been the means of enriching chemistry with several new metals. It has further demonstrated that some elements which were formerly believed to have been obtained in a state of purity have in reality been contaminated with foreign matter: a state of things which has rendered necessary a revision of some of the atomic weights. But the achievement of spectrum analysis which appeals most powerfully to the imagination is the creation of an entirely new branch of chemical science, that of *celestial chemistry*, in which, by the application of the spectroscope to the examination of the light emitted by solar and stellar matter, chemists have been enabled to prove the presence of many of our terrestrial elements in the sun and stars. In addition to this, the spectroscope has furnished us with information concerning the physical constitution of these luminaries, and even concerning their rate of motion, which would formerly have been deemed unattainable.

The form of spectroscope most generally employed for chemical purposes is represented in Fig. 48. The rays of light to be examined pass through a vertical slit situated at the end of the tube A, and turned from the spectator in the diagram. After being rendered parallel by means of a lens, they fall upon the prism P. The spectrum is viewed directly by means of the telescope B. In this way it is

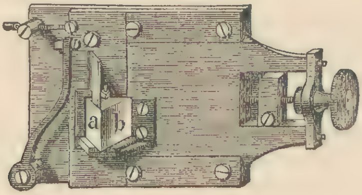
not only magnified, but is made to exhibit a greater degree of sharpness of detail than it would possess if thrown upon a screen. The tube C carries a transparent horizontal graduated scale, which is illuminated by a small luminous gas-flame placed at the end of the tube and not

Fig. 48.



represented in the diagram. In looking through the telescope this scale is seen reflected in the face P of the prism. In this way it is viewed simultaneously with the spectrum, the various parts of which may thus be referred to the divisions of the graduated scale. In order to compare light from two different sources, one half of the slit, which is represented on a larger scale in Fig. 49, is covered by a small prism *ab*. The light from one source, F, Fig. 48, situated in front of the

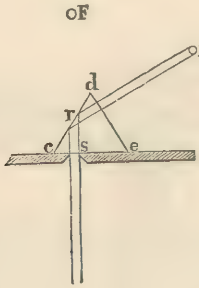
Fig. 49.



slit passes directly through the uncovered half of the slit; the light from the second source, *f*, which must be placed to the side of the slit, passes through the covered portion of the slit by total reflection in the small prism. Various arrangements of the small prism are employed for this purpose; one of the simplest is that represented in Fig. 50. The light from *f*, Fig. 50, enters the equilateral prism *cde* perpendicularly to the face *de*, is totally reflected at *r* from *cd*, and emerging from the prism perpendicularly to *ce*, enters the slit *s*. As the direction of the rays of light on entering and on quitting the prism is perpen-

dicular to the faces of the prism, no refraction occurs with this prism. At the same time the light from F cannot enter the slit through the prism, and can pass only through the uncovered portion of the slit. In this way the two spectra from the two sources of light may be viewed simultaneously, one above the other, and as in both spectra the light

FIG. 50.



passes through the same slit and is refracted by the same prism P, there will be perfect correspondence of the similar parts of each: rays of the same wave-length will be found in the same vertical line in the two spectra, and thus coincidences may be observed and studied.

In order to understand the principles upon which spectrum analysis is based, it will be necessary to consider what is the precise nature of the phenomena observed when bodies are heated to the temperature at which they become self-luminous. If a liquid or a solid be thus gradually heated, and at the same time examined with the spectroscope, the red end of the spectrum will be observed first. The body is then at a low red heat. As the temperature rises, the orange rays will be added; then the yellow, and so on from the less refrangible to the more refrangible rays, until the entire visible spectrum from red to violet can be seen. The body is then white-hot, and the white light which it emits is thus seen to be compounded of every wave-length in the visible spectrum.* The spectra of glowing solids and liquids are therefore continuous. The molecules of solids and liquids are hampered by cohesion, and are not free to take up those vibrations which are peculiar to them. We may conceive that in different parts of the mass cohesion is overcome to a varying extent at the same time, and that molecular groupings of every possible degree of variety and complexity are vibrating, each with its specific rate of vibration. We should thus have the simultaneous emission of light of every wave-length—of every degree of refrangibility.

Gases or vapors behave otherwise. Their molecules are free to oscillate unimpeded by each other; and the molecules of any one element, being all of the same kind, execute at a given temperature vibrations

* In addition to the visible spectrum, there is an invisble region of rays of lower refrangibility than the red—the *infra-red* rays—and a second invisible region of rays of higher refrangibility than the violet—the *ultra-violet* rays. These two invisible portions, which lie on either side of the visible spectrum, have by the aid of photography been rendered accessible to spectroscopic study.

identical in nature and in velocity, and consequently, if heated to the temperature at which they become self-luminous, emit light of definite wave-lengths and therefore of definite color, not a mixture of light of all wave-lengths, or white light. Every element, therefore, in the state of self-luminous vapor, and at a temperature sufficiently high, displays a spectrum peculiar to itself, and consisting of definite lines or bands. The dark spaces between these lines or bands correspond to those wave-lengths of light which the atoms or molecules of the element do not excite.

In this way the spectroscopic examination of the elements in the condition of self-luminous vapor affords a means of distinguishing between them—a means more expeditious, less liable to misinterpretation, and, as we shall see presently, more delicate than the ordinary chemical tests. The identification of the elements by means of the spectroscope is greatly facilitated by the arrangement for comparing spectra already described (p. 401). For example, if the spectrum of a substance under examination appears to be that of barium, it is only necessary to examine, simultaneously with this spectrum, the spectrum of an actual specimen of barium by means of the comparing prism : the coincidence or non-coincidence of the lines in the two spectra will at once inform us whether our surmise is correct, or the reverse.

The metallic vapors for examination may in many cases be obtained by heating the metal or its compounds in the Bunsen flame. Sometimes, however, a higher temperature is necessary, in which case the electric arc or the induction spark may be employed as the source of heat. In the case of metals, it is sufficient to pass the spark between poles of the metal, when a sufficient quantity is volatilized to give a spectrum. It is to be borne in mind, however, that in this method the spectra of the gases through which the spark passes (oxygen, nitrogen, etc.) will also be visible.

As regards the certainty of identification of the elements by spectroscopic means, a noteworthy point is the ease with which metallic vapors, the colors of which appear to the eye almost or entirely identical, may be discriminated with the aid of the spectroscope. The red colors which lithium and strontium compounds respectively impart to the Bunsen flame, though distinguishable by a trained eye, are yet extremely similar; but the flame spectrum of lithium consists of a bright red line and a very weak line in the yellow, whilst that of strontium contains several lines in the red, one in the orange, and one in the blue. The flame colors of the compounds of potassium, cæsium, and rubidium are to the eye absolutely identical, and there are, moreover, no characteristic qualitative tests by which the compounds of these elements may be distinguished, but their spectra present the most marked differences. So similar are these elements, that it is probable that by chemical means alone cæsium and rubidium could never have been discovered. Indeed cæsium had, previous to its spectroscopic recognition as a distinct element, been confounded with potassium (see Cæsium).

The delicacy of the spectroscopic tests for the elements is due to the minuteness of the quantity of self-luminous vapor necessary to impart to the luminiferous ether a perceptible impulse. The highest degree

of delicacy is manifested in the case of sodium, a quantity of which less than the $\frac{1}{3000000000}$ of a gram may be detected. This almost inconceivable delicacy is due to two causes: in the first place the spectrum of sodium consists of one double line in the yellow, hence the entire effort of the atoms is concentrated upon one part, and that the most luminous of the spectrum; and, secondly, the atomic weight of sodium is low, so that a smaller quantity is required to produce an effect. Thallium also gives only one line, but it is in the green —a portion of the spectrum which affects the eye less powerfully; and the atomic weight of thallium is high; hence the reaction is in this case less delicate. In the case of lithium $\frac{1}{5000000}$ of a gram may be detected. With the induction spark $\frac{1}{750000000}$ of a gram of copper gives a brilliant spectrum, and 0.2 of a milligram of copper keeps up this spectrum for six hours.

In identifying an element by means of its spectrum, it is not necessary that every line in the spectrum should be perceived. In almost all spectra there are certain lines brighter than the rest, and these are frequently visible when the quantity of substance vaporized is insufficient for the perceptible production of the fainter lines. The presence of one of these prominent or characteristic lines is sufficient for the identification of an element.

Nearly all metallic compounds are decomposed into their elements at a temperature below that at which their vapors become luminous. On this account the spectra of the compounds of the metals with the non-metals are frequently the same as those of the metals themselves.* But this is not always the case, especially at comparatively low temperatures. Thus copper and cuprous chloride give the same spectrum in the electric arc, but not in the Bunsen flame. In many such cases there is a temperature at which a compound gives its own peculiar spectrum plus that of each of its elements.

When no chemical combination occurs, spectra of any number of elements can co-exist side by side without confusion. In this way the qualitative analysis of mixed materials may be safely made. It is only necessary to identify in the mixed spectrum the more characteristic lines of the various elements.

Gases which under ordinary pressures give a line spectrum behave otherwise under high pressures. As the pressure increases, the lines gradually broaden, until ultimately the spectrum becomes continuous. This is again a case in which the freedom of atomic vibration is interfered with by the too great proximity of the atoms to each other.

All bodies capable of vibration possess the power of taking up or absorbing those waves which they would cause by their own vibration. Thus a finger-glass may be made to sound by singing its own note close to it. The same law holds with regard to the vibrating atoms

* The non-metals require a higher temperature than many of the metals in order that they may exhibit their characteristic spectra. Thus in the case of the decomposed compound of a metal with a non-metal, it frequently happens, as above stated, that the spectrum of the metal alone is visible.

and molecules of a gas. If we examine with a spectroscope a source of white light yielding a continuous spectrum—a white-hot solid or liquid —and then introduce between the slit of the spectroscope and the source of white light, a layer of sodium vapor, then according to the relative temperatures of the source of white light and the sodium vapor, one of three things will happen: either the sodium vapor is hotter—*i.e.*, possesses greater energy of atomic vibration—than the white-hot solid or liquid, in which case it will emit more yellow light than it receives from the latter, and a bright yellow sodium line will be visible in the otherwise continuous spectrum; or it is of the same temperature, when it will emit just as much as it receives, and only the continuous spectrum will be seen; or, finally, it is colder, in which case it will absorb more than it emits, and a *dark* sodium line will be visible on the background of the continuous spectrum. This is in accordance with the *law of exchanges.* Its chief importance in connection with the present subject lies in the explanation which it affords of the phenomena observed in the spectroscopic study of the heavenly bodies.

Solar and Stellar Spectra.—If the light from the sun be examined spectroscopically, the phenomena observed do not correspond either with those of an incandescent gas, or with those of an incandescent solid or liquid. The visible solar spectrum consists of a band of colored light stretching from the red to the violet; but this colored spectrum is crossed by a vast number of fine dark lines. These lines were first observed by Wollaston. They were afterwards mapped by Fraunhofer, a German optician, for which reason they are known as the Fraunhofer lines.

If we examine simultaneously by means of the comparing prism the solar spectrum and the spectrum of a metallic element, we find that in the case of many metallic elements, such, for example, as iron or calcium, every bright line in the spectrum of the metallic element corresponds in position, breadth, and intensity with a dark line in the solar spectrum.

We have already seen that the bright line of sodium may be *reversed* and converted into a dark line. The dark lines in the solar spectrum have a similar origin. In the sun, we have in the first place an incandescent nucleus, solid or liquid, the source of light, and capable of yielding a continuous spectrum. Owing to the high temperature of the sun, the elements, of which the mass of this luminary is composed, are in part volatilized, and we have thus an atmosphere of incandescent vapor surrounding the incandescent nucleus. Through this atmosphere all light from the nucleus must pass. The temperature of the solar atmosphere is necessarily lower than that of the nucleus; hence metallic vapors contained in this atmosphere absorb more light than they emit, and the lines of their spectra consequently appear dark on the continuous spectrum of the nucleus. The nucleus of the sun is distinguished as the *photosphere;* its atmosphere, in which this selective absorption occurs, as the *chromosphere.* Under certain conditions it is possible to submit the light from the chromosphere alone to spectroscopic examination, and in this case a spectrum of bright lines on a dark ground, corresponding with that of a glowing gas, is obtained.

The origin of the dark lines in the solar spectrum was first satisfac-

torily explained by Kirchhoff, who verified his theory by an elaborate series of observations. The same explanation had, however, been previously suggested by Stokes.

The alternative hypothesis, that the coincidence of the bright lines of the spectra of the metallic elements with the dark lines of the solar spectrum is due to chance, and not to the presence of these elements in the solar atmosphere, is untenable. In the case of the spark spectrum of iron, Angström has counted no fewer than 460 lines, each of which coincides with a dark line in the solar spectrum. The probability of 460 chance coincidences in the spectrum of one metal is inconceivably small; and, when we take into account the fact already mentioned, that the coincidence of the lines is one not merely of position, but in every case one also of breadth and intensity, this small probability becomes still further diminished. We must therefore conclude that the various elements which yield these lines are really present in the solar atmosphere.

The following is a list of the metallic elements which have thus been detected in the atmosphere of the sun:

H, Na, K, Rb, Cs, Li, Ba, Sr, Ca, Mg, Al, Cr, Be, Ce, La, Yt, Zn, Mn, Ni, Co, Fe, U, V, Pb, Bi, Cu, Cd, Pd, Ir, Sn, Mo, Ti.

The spectroscopic study of the stars has afforded much information concerning the constitution of these bodies. The moon and planets exhibit the same spectrum as the sun, which is in accordance with the fact that they shine by the reflected light of that luminary. The fixed stars are found to be bodies constituted like our sun, although differing greatly both from the latter and from each other. The spectra of the greater number display dark lines. Many terrestrial elements have already been detected in the stars. Thus Aldebaran contains hydrogen, sodium, magnesium, calcium, iron, tellurium, antimony, bismuth, and mercury; whilst in Sirius sodium, magnesium, and hydrogen have been detected.

The spectra of the irresolvable nebulæ, on the other hand, display *bright* lines. This shows that these nebulæ consist of masses of incandescent gas, without a solid or liquid nucleus—a discovery which affords powerful support to the Kant-Laplace hypothesis of the origin of the solar system.

Relations of the Metals to Gravity.

Specific Gravity of Metals.—A table of specific gravities of substances consists of a series of numbers indicating the relative quantities of matter contained in equal volumes of these substances. The measure of the quantity of matter is, *cœteris paribus*, the weight. Since in the case of solids and liquids the specific gravity of water at 4° C. is taken as unity, we may put it that the number expressing the specific gravity of a solid or liquid substance indicates the number of times that a given volume of this substance is heavier (or lighter) than an equal volume of water at 4° C. For an account of the methods by which the specific gravity is determined a work on physics must be consulted; but the following relation, which is useful to remember, may be mentioned

here: The number expressing the specific gravity of a solid or liquid also expresses the weight in grams of one cubic centimetre of the substance measured at the temperature at which the specific gravity was determined. This is due, in the first place, to the fact that, in the metric system, the unit of weight is the weight of the unit of volume of water at 4° C. (1 cubic centimetre of water at 4° C. weighs 1 gram); and, secondly, to the fact above mentioned, that the specific gravities of solids and liquids are referred to that of water at 4° C. as unity.

The metals exhibit a very wide range in their specific gravities, varying from 0.594 in the case of lithium, the lightest of known solids, to 22.477 in the case of osmium, the heaviest.

The following table contains the specific gravities of some of the more important metals:

Name of Metal.	Sp. gr.
Osmium,	22.477
Iridium,	22.40
Platinum,	21.50
Gold,	19.26
Mercury,	13.596
Lead,	11.37
Silver,	10.47
Copper,	8.95
Cadmium,	8.66
Iron,	7.79
Tin,	7.29
Zinc,	6.92
Aluminium,	2.67
Magnesium,	1.74
Sodium,	0.974
Potassium,	0.865
Lithium,	0.594

Cohesive Power.

The properties of matter which are dependent upon cohesion, that is to say, upon the mutual attraction of the molecules of a substance, are *tenacity*, *hardness*, *brittleness*, *malleability*, and *ductility*. These very important properties are possessed by the various metals in very different degrees. Upon them depends the value or otherwise of the metals for the purposes of art and manufacture.

The *tenacity* of a substance is the resistance which that substance opposes to the separation of its parts. This separation may be sought to be effected either by strain or by crushing weight. The tenacity of a metal towards strain may be determined by suspending weights by a wire of the metal, and noting the weight sufficient to cause rupture. By repeating this operation with wires of different metals, care being taken that the wires are, in every case, of equal cross-section, a table of relative tenacities may constructed. In the following table the tenacity of lead is taken as unity:

Relative Tenacity of Metals.

Lead,	1
Tin,	1.3
Zinc,	2
Palladium,	11.5
Gold,	12
Silver,	12.5
Platinum,	15
Copper,	18
Iron,	27.5
Nickel,	41.2
Steel,	42

This means that if a lead wire of given thickness willl support, as maximum load, say 1 kilogram, a steel wire of the same thickness will support 42 kilograms. The tenacity of cobalt is greater than that of iron. The tenacity of most metals is diminished by annealing; that is, by heating the metal and allowing it to cool slowly.

Resistance to strain and to crushing weight are distinct properties. Thus the three kinds of iron range as follows in regard to their order of tenacity:

Strain.	Crushing weight.
Wrought iron.	White cast iron.
Gray cast iron.	Gray cast iron.
White cast iron.	Wrought iron.

Hardness is the resistance which a substance opposes to penetration, or to change of form generally. It is not easy to determine hardness with quantitative accuracy; but we may readily ascertain which of two substances is the harder by endeavoring to scratch the one with the other. In this way a scale of standard substances has been prepared, each of which is harder than its predecessor:

Scale of Hardness. (Mohs.)

1. Talc.	6. Felspar.
2. Gypsum or rock salt.	7. Quartz.
3. Calcite.	8. Topaz.
4. Fluorspar.	9. Corundum.
5. Apatite.	10. Diamond.

Thus, a substance which scratches fluorspar but is scratched by apatite, has a hardness lying between 4 and 5. The numerals denote simply order, not degree of hardness. This scale is much employed by mineralogists.

Among the metals, titanium, manganese, chromium, and ruthenium are so hard as to scratch glass, whilst sodium may be moulded with the fingers. The native alloy of osmium and iridium is exceedingly hard, and is employed on this account in the manufacture of the nibs of gold pens.

Brittleness is the incapacity of a substance to undergo change of form —by bending, hammering, or otherwise—without rupture. Among the

metals, brittleness is generally associated with a crystalline structure; the crystalline metals, antimony, arsenic, and bismuth, fly into fragments under the hammer. Tenacious metals frequently possess a fibrous structure. Thus, the highly tenacious metals, wrought iron and wrought copper, are fibrous, as may be seen by fracturing a bar of the metal by repeated bending and observing the surface of fracture; whereas, cast iron and *slowly* deposited electrolytic copper are crystalline and brittle. Fibrous wrought iron, when kept in a state of vibration for a great length of time, undergoes a slow molecular rearrangement whereby the fibrous structure becomes crystalline. To this cause is sometimes due the snapping of the axles of railway carriages and of the shafts of screw steamers.

Malleability and Ductility.—Malleability is the property of being reducible to thin leaves, either by hammering or by passing between rollers. The most malleable of the metals is gold; it has been beaten into leaves $\frac{1}{282000}$th of an inch in thickness. 1 square decimetre of this leaf weighs less than 20 milligrams. Silver and copper may also be hammered into thin leaf. The remaining metals in the accompanying table may be reduced to thin foil by rolling, but not by hammering:

Order of Malleability.

1. Gold.
2. Silver.
3. Copper.
4. Tin.
5. Platinum.
6. Lead.
7. Zinc.
8. Iron.

Ductility is the capability of being drawn into wire. The metal is first formed into rods; these are then drawn through holes in a steel draw-plate. The holes, through which the wire passes, diminish in size by regular gradation. The process of drawing is continued until the requisite degree of tenuity is attained. Sometimes it is necessary to anneal the wire from time to time during the process of drawing. Very fine gold and silver wire is drawn through an aperture in a ruby. Most malleable metals are ductile, but in an order somewhat different from that of their malleability:

Order of Ductility.

1. Gold.
2. Silver.
3. Platinum.
4. Iron.
5. Copper.
6. Palladium.
7. Aluminium.
8. Zinc.
9. Tin.
10. Lead.

Thus iron, by virtue of its superior tenacity, is more ductile than some of the more malleable metals. A non-malleable metal cannot be ductile. Gold wire has been drawn $\frac{1}{5000}$th of an inch in diameter. Wires of gold and platinum have been obtained by Wollaston $\frac{1}{30000}$th of an inch in diameter. This extraordinary degree of tenuity was attained by placing a wire of gold or platinum in the axis of a cylinder of silver, then drawing the compound wire in the ordinary way and dissolving off the silver with nitric acid. Soft metals, such as sodium and potassium, may be obtained in the form of wire by forcing them through an aperture in a steel die. This has of course nothing to do with the true ductility of these metals: the wires are pressed, not drawn. True ductility, as above stated, is dependent to a great extent upon tenacity.

The properties of malleability and ductility vary in each metal with the temperature. Copper is tough and malleable at ordinary temperatures; but at a temperature approaching its fusing-point it becomes so brittle that it may be reduced to powder. In reference to this property copper is said to be "hot short." The behavior of zinc in this respect is peculiar: at ordinary temperatures it is moderately brittle: between 100° and 150° C. (212°–262° F.) it is so malleable and ductile that it may be wrought with facility: whilst at 205° C. (401° F.) it is more brittle than at ordinary temperatures, and may be pulverized in a mortar.

Alloys.

Many metals, when fused along with others, unite with these to form a homogeneous metallic mass known as an alloy. In some such cases chemical combination appears to take place: thus the union of sodium with mercury is accompanied with evolution of heat and light; in others the combination is merely one of mutual solution. The chemical compounds which are formed are difficult to isolate, as they are generally soluble in all proportions in an excess of any of the constituents. The best characterized chemical compounds are always those which result from the union of elements differing most widely in their properties—thus of the most positive with the most negative elements; and in such compounds the properties of the constituent elements are obliterated. The metals, on the other hand, standing, as they do, near to each other in the electrochemical scale, form compounds which are devoid of sharply-defined characteristics, and in which the properties of the constituent metals are preserved. Thus all alloys possess metallic lustre, and are good conductors of heat and electricity.

Very few pure metals possess properties which fit them, as such, for use in the arts. Thus pure copper is soft, and cannot be worked on the lathe. By alloying it with zinc it is converted into the hard and workable brass. In like manner before gold and silver can be coined, these metals must be alloyed with a certain percentage of copper in order to impart to them the necessary hardness and durability. Thus the properties—sometimes even the defects—of one metal are employed to correct or modify those of another in the preparation of alloys.

Alloys of metals with mercury are known as *amalgams* (*q.v.*).

The properties of the various alloys will be treated of later on in connection with one or other of their constituent metals.

The law regulating the fusing-point of alloys has already been referred to (p. 399).

CHAPTER XXXII.

MONAD ELEMENTS.

SECTION III.

POTASSIUM, K_2?

Atomic weight = 39. *Probable molecular weight* = 78. *Sp. gr.* 0.865. *Fuses at* 62.5° C. (144.5° F.). *Boils at a low red heat.* *Atomicity* ′. *Evidence of atomicity:*

Potassic chloride, ...	KCl.
Potassic iodide, ...	KI.
Potassic hydrate, ...	KHo.
Potassic sulphide, ...	$\mathbf{S}K_2$.

History.—Potassium was first isolated in 1807 by Davy, who obtained it by the electrolysis of potassic hydrate.

Occurrence.—The salts of potassium are widely distributed in nature. Double silicates of potassium with aluminium and other metals form a variety of important minerals, which are among the proximate constituents of the igneous rocks. By the disintegration of these rocks soils are produced. From the soils the potassium is absorbed by plants, in the juices of which it occurs as the potassium salts of organic acids. From plants it passes into the bodies of animals.

Further, in the inorganic world, the chloride, bromide, and iodide of potassium are found in sea-water, in mineral springs, and in solid saline deposits, whilst the nitrate occurs in tropical climates as an efflorescence on the soil.

Preparation.—1. When a piece of solid potassic hydrate, slighly moistened in order to increase its conducting power, is placed between the poles of a powerful voltaic battery, decomposition takes place according to the following equation:

$$\underset{\text{Potassic hydrate.}}{2\mathbf{O}KH} = K_2 + H_2 + O_2.$$

Potassium and hydrogen are liberated at the negative pole. The potassium forms metallic globules which inflame in contact with air, and must be removed and preserved under petroleum.

This was the method of preparation originally employed by Davy.

2. Potassium may also be obtained by the action of metallic iron on potassic hydrate at a strong white heat:

$$\underset{\substack{\text{Potassic}\\\text{hydrate.}}}{4\mathbf{O}KH} + 3Fe = \underset{\substack{\text{Magnetic iron}\\\text{oxide.}}}{{}^{iv}(\mathbf{Fe}_3)^{viii}O_4} + 2K_2 + 2H_2.$$

3. The most convenient method of preparing potassium consists in heating potassic carbonate to a white heat with charcoal. Hydric potassic tartrate (cream of tartar) is first ignited in a closed crucible, when the following decomposition takes place:

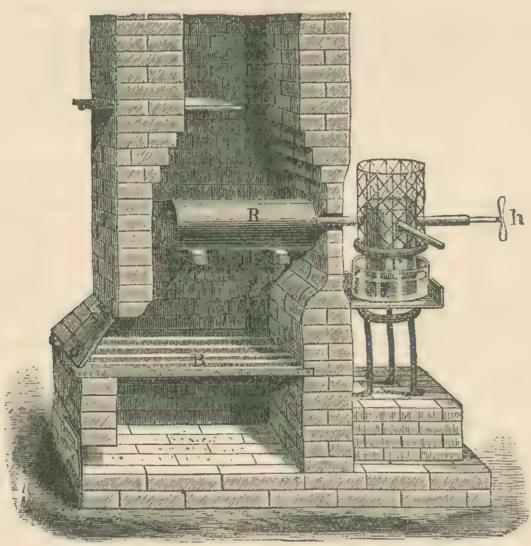
$$\underset{\substack{\text{Hydric potassic}\\\text{tartrate.}}}{2\left\{\begin{matrix}\mathbf{C}OKo\\ \mathbf{C}HHo\\ \mathbf{C}HHo\\ \mathbf{C}OHo\end{matrix}\right.} = \underset{\substack{\text{Potassic}\\\text{carbonate.}}}{\mathbf{C}OKo_2} + \underset{\text{Water.}}{5\mathbf{O}H_2} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{4\mathbf{C}O} + 3C.$$

The residue, consisting of potassic carbonate and finely divided carbon, is mixed with charcoal and distilled at a white heat from an iron retort R (Fig. 51):

$$\underset{\substack{\text{Potassic}\\\text{carbonate.}}}{\mathbf{C}OKo_2} + 2C = \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{3\mathbf{C}O} + K_2.$$

The vapor of potassium condenses in a copper receiver *r*, from which air is excluded. If the neck of the retort becomes choked during the pro-

FIG. 51.



cess, it may generally be cleared by means of an iron rod *h*, introduced through the lateral tube of the receiver. Should this fail, the fire-bars

B, which are movable, must be withdrawn, so as to allow the fire to fall on to the hearth.

The potassium obtained by the above process is contaminated with carbonic oxide, from which it must be freed by redistillation. A neglect of this precaution may lead to dangerous accidents, as when the crude potassium is preserved, even under petroleum, a black powder is formed which explodes violently on the slightest friction.

Properties.—Potassium is a silvery-white metal, brittle and crystalline at 0° C, but at ordinary temperatures soft like wax. The freshly cut surface of the metal has a brilliant lustre, which it almost instantly loses when exposed to air, owing to the formation of oxide. For this reason it is necessary to keep the metal immersed in some liquid devoid of oxygen, such as petroleum. When heated in air it inflames and burns with a violet light, forming a mixture of peroxides of potassium.

By melting potassium in a sealed tube filled with coal-gas, allowing the metal partially to solidify, and then pouring off the liquid portion, well formed crystals of potassium may be obtained.

Reactions.—1. Potassium decomposes water, even at its freezing point, with great energy, the heat evolved being sufficient to cause the ignition of the liberated hydrogen:

$$\underset{}{K_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{2KHo} + H_2.$$

2. It inflames spontaneously in an atmosphere of chlorine. It also inflames when brought in contact with bromine, the reaction taking place with explosive violence. In these cases potassic chloride (KCl) and bromide (KBr) are formed.

3. When potassium is ignited in a stream of carbonic anhydride, a portion of the latter is reduced, with liberation of carbon:

$$2K_2 + \underset{\substack{\text{Carbonic}\\ \text{anhydride.}}}{3\mathbf{C}O_2} = \underset{\substack{\text{Potassic}\\ \text{carbonate.}}}{2\mathbf{C}OKo_2} + C.$$

Uses.—Owing to its powerful affinity for electro-negative elements, potassium is employed in the laboratory to expel elements, less strongly electro-positive than itself, from their combinations with electro-negative elements. Thus, by its means, boron and silicon may be prepared from their oxides, and aluminium, magnesium, and other metals from their chlorides. The more readily obtainable sodium has, however, almost totally superseded it for these purposes.

COMPOUND OF POTASSIUM WITH HYDROGEN.

Potassic hydride, K_4H_2.—When potassium is heated in a current of pure hydrogen, the gas is absorbed by the metal, and potassic hydride is formed. The absorption begins at 200° C. (392° F.), and is most rapid about 300° C. (572° F.). The hydride is a brittle crystalline mass, with a silvery metallic lustre. It may be fused in an atmosphere of hydrogen. Under ordinary pressures it may be heated to 410° C. (770° F.) without change, but in a vacuum it begins to dissociate at 200° C. (392° F.). It inflames spontaneously in conact with air.

COMPOUNDS OF POTASSIUM WITH THE HALOGENS.

POTASSIC CHLORIDE, KCl, occurs native in saline deposits as the mineral *sylvine.* In smaller quantities it is found in sea-water and in brine-springs. It crystallizes in colorless cubes, and possesses a saline taste. It dissolves in 3 parts of water at ordinary temperatures, and is more soluble at higher temperatures. Alcohol does not dissolve it. It forms molecular compounds—double salts—with various other metallic chlorides. *Potassic platinic chloride* (*potassic chloroplatinate*), $\mathbf{Pt}Cl_4,2KCl$, is obtained as a granular precipitate, consisting of minute octahedra, when solutions of the two chlorides are mixed. This salt is almost insoluble in cold water, and is used in the quantitative determination of potassium.

POTASSIC BROMIDE, KBr, forms colorless cubes of sp. gr. 2.69, readily soluble in water, slightly soluble in alcohol.

POTASSIC IODIDE, KI, is prepared by digesting iron filings, water, and iodine together, filtering the colorless solution, and precipitating the iron by potassic carbonate:

$$Fe + I_2 = \underset{\text{Ferrous iodide.}}{\mathbf{Fe}I_2};$$

$$\underset{\text{Ferrous iodide.}}{\mathbf{Fe}I_2} + \underset{\text{Potassic carbonate.}}{\mathbf{CO}Ko_2} = \underset{\text{Potassic iodide.}}{2KI} + \underset{\text{Ferrous carbonate.}}{\mathbf{CO}Feo''}.$$

It crystallizes in cubes of sp. gr. 2.9. It dissolves at ordinary temperatures in 0.7 part of water and in 40 parts of alcohol. The aqueous solution dissolves large quantities of iodine. Potassic iodide forms molecular compounds with many other metallic iodides.

POTASSIC FLUORIDE, KF, is obtained by neutralizing hydrofluoric acid with potassic carbonate. At ordinary temperatures it is deposited from its solutions in crystals of the formula $KF,2\mathbf{O}H_2$, but above 35° C. (95° F.) it crystallizes in anhydrous cubes. It is deliquescent. The solution attacks glass. It forms numerous double fluorides: the so-called acid fluoride has the formula KF,HF. *Potassic silicofluoride,* SiF_6K_2 ($= \mathbf{Si}F_4,2KF$), which is formed as a gelatinous precipitate when hydrofluosilicic acid is added to the solution of a potash salt, may also be regarded as belonging to this class.

COMPOUNDS OF POTASSIUM WITH OXYGEN.

Potassic oxide, ...	$\mathbf{O}K_2$.	K—O—K.
Potassic dioxide, ...	$\left\{\begin{matrix}\mathbf{O}K\\ \mathbf{O}K\end{matrix}\right.$.	K—O—O—K.
Potassic tetroxide, ...	$\left\{\begin{matrix}\mathbf{O}K\\ O\\ O\\ \mathbf{O}K\end{matrix}\right.$.	K—O—O—O—O—K.

POTASSIC OXIDE, OK_2, is formed by the spontaneous oxidation of potassium at ordinary temperatures in dry air. It may also be obtained by heating potassic hydrate with potassium:

$$\underset{\text{Potassic hydrate.}}{2KHo} + K_2 = \underset{\text{Potassic oxide.}}{2OK_2} + H_2;$$

or by fusing together, in a current of nitrogen, potassic peroxide and potassium.

Potassic oxide is white, fusible, and, at high temperatures, volatile. It is very deliquescent, and combines violently with water to form potassic hydrate. When moistened with water it becomes incandescent.

POTASSIC DIOXIDE, K_2O_2, is formed with evolution of oxygen when the tetroxide is dissolved in water.

POTASSIC TETROXIDE, *Potassic peroxide*, K_2O_4, is prepared by fusing potassium in a current of oxygen. It is a chrome-yellow powder. Water decomposes it as above (see *Potassic dioxide*).

COMPOUND OF POTASSIUM WITH HYDROXYL.

POTASSIC HYDRATE, *Caustic potash, Potash*, KHo or OKH, is prepared by boiling in an iron vessel a solution of potassic carbonate with calcic hydrate:

$$\underset{\text{Potassic carbonate.}}{COKo_2} + \underset{\text{Calcic hydrate.}}{CaHo_2} = \underset{\text{Potassic hydrate.}}{2KHo} + \underset{\text{Calcic carbonate.}}{COCao''}.$$

1 part of potassic carbonate is dissolved in 12 parts of water, and milk of lime is added till a sample of the filtered liquid no longer effervesces when treated with an acid. (With a concentrated solution of the carbonate, the reaction does not take place; in fact a concentrated solution of potassic hydrate decomposes calcic carbonate with formation of potassic carbonate and calcic hydrate.)

The clear solution of potassic hydrate is decanted from the precipitate of calcic carbonate, and is concentrated, first in a covered iron pot, and afterwards in a silver basin, until all the water has been driven off and the fused oily hydrate remains. This solidifies on cooling to a crystalline mass.

It is also formed by the action of potassium upon water (see p. 413) and by dissolving potassic oxide in water:

$$OK_2 + OH_2 = 2OKH.$$

Properties.—Potassic hydrate is a hard white brittle substance, with a slightly fibrous fracture. It fuses below a red heat, and at higher temperatures volatilizes without decomposition. It is very deliquescent. It dissolves in about half its weight of water, yielding a highly caustic solution, which, when exposed to the air, rapidly absorbs carbonic anhy-

dride. Hot concentrated solutions deposit on cooling quadratic plates, or octahedra, of the formula $KHo,2OH_2$, readily soluble in alcohol.

Reactions.—By contact with acids, potassic hydrate produces potassium salts:

$$\underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{KHo} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl} = \underset{\substack{\text{Potassic}\\ \text{chloride.}}}{KCl} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{KHo} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{SO_2Ho_2} = \underset{\substack{\text{Hydric potassic}\\ \text{sulphate.}}}{SO_2HoKo} + \underset{\text{Water.}}{OH_2}.$$

$$\underset{\substack{\text{Potassic}\\ \text{hydrate.}}}{2KHo} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{SO_2Ho_2} = \underset{\substack{\text{Potassic}\\ \text{sulphate.}}}{SO_2Ko_2} + \underset{\text{Water.}}{OH_2}.$$

OXY-SALTS OF POTASSIUM.

POTASSIC NITRATE, *Nitre, Saltpetre,* NO_2Ko. (*Occurrence, formation, nitre plantations,* see p. 214.) Nitre is manufactured in large quantities from Chili saltpetre (sodic nitrate) by the double decomposition of the latter salt with potassic chloride. Equal molecular proportions of the two salts are dissolved in hot water until the specific gravity of the solution attains to 1.5. Sodic chloride, which is almost equally soluble in hot and in cold water, separates out, whilst the solution deposits potassic nitrate on cooling. The product is technically known as "converted nitre." Potassic nitrate is dimorphous. It crystallizes most frequently in longitudinally striated six-sided prisms belonging to the rhombic system, but may also be obtained in minute rhombohedra, isomorphous with those of sodic nitrate. It has a cooling saline taste. It dissolves in four times its weight of cold water, and in a third of its weight of boiling water, but is insoluble in alcohol. It fuses at 339° C., and at a red heat is decomposed with evolution of oxygen and formation of potassic nitrite. At a very high temperature it is converted into potassic oxide. Owing to its property of thus parting with oxygen, it oxidizes most of the elements when heated with them, frequently with explosive violence.

Gunpowder.—Gunpowder is a mixture of 75 parts of nitre, 10 parts of sulphur, and 15 parts of charcoal. The composition varies, however, in different countries, and also according to the purpose for which the powder is intended. The separate ingredients are finely powdered, then intimately mixed, adding a small quantity of water; the mixture is pressed by hydraulic power into a hard cake, which is then granulated. The grains are sorted according to size, polished, and finally dried. The principal products of the combustion of gunpowder are nitrogen, carbonic anhydride (with traces of carbonic oxide), potassic sulphate, and potassic carbonate. The explosive force of gunpowder is due to the sudden evolution of gases occupying a volume several hundred times greater than that of the original substance.

Potassic nitrite, $NOKo$, is prepared by fusing the nitrate, either alone or with lead, the oxidizable metal serving to remove the oxygen from the nitrate. The mass is extracted with water, and the solution evaporated and allowed to crystallize. The unchanged nitrate separates out first, whilst the nitrite remains in the mother liquor, from which it may be obtained by further evaporation in small prismatic deliquescent crystals. It is insoluble in absolute alcohol.

POTASSIC CHLORATE, $\left\{\begin{matrix} \mathbf{O}Cl \\ \mathbf{O}Ko \end{matrix}\right.$. (Preparation, p. 182.) This salt forms lustrous tabular crystals belonging to the monoclinic system, soluble in 16 parts of cold, and in 2 parts of boiling water. It fuses at 334° C. (633° F.), and is decomposed at 352° C. (666° F.) into oxygen, potassic chloride, and potassic perchlorate. At a still higher temperature it parts with the whole of its oxygen, and is converted into potassic chloride (pp. 184 and 161).

It is a powerful oxidizing agent, and, along with sulphur or antimonious sulphide, forms detonating mixtures which explode by percussion or friction, owing to the sudden combustion of the oxidizable ingredient at the expense of the oxygen of the potassic chlorate.

POTASSIC PERCHLORATE, $\left\{\begin{matrix} \mathbf{O}Cl \\ O \\ \mathbf{O}Ko \end{matrix}\right.$ (Preparation, p. 184), crystallizes in rhombic prisms, soluble in 70 parts of cold, in 6 parts of boiling water, insoluble in alcohol. When heated to about 400° C. (752° F.) it is decomposed into oxygen and potassic chloride.

Potassic bromate, $\left\{\begin{matrix} \mathbf{O}Br \\ \mathbf{O}Ko \end{matrix}\right.$, is best prepared by passing chlorine into an aqueous solution of 1 mol. of bromine with 6 molecules of potassic carbonate:

$$\underset{\text{Potassic carbonate.}}{6\mathbf{C}OKo_2} + 5Cl_2 + Br_2 = \underset{\text{Potassic bromate.}}{2\left\{\begin{matrix} \mathbf{O}Br \\ \mathbf{O}Ko \end{matrix}\right.} + \underset{\text{Potassic chloride.}}{10KCl} + \underset{\text{Carbonic anhydride.}}{6CO_2}.$$

(See also p. 319.) It crystallizes in rhombohedra, sparingly soluble in water. It resembles in its properties the chlorate.

Potassic iodate, $\left\{\begin{matrix} \mathbf{O}I \\ \mathbf{O}Ko \end{matrix}\right.$.—Chlorine is passed into water, in which iodine is suspended, until all the iodine dissolves. Potassic chlorate is then added, when potassic iodate is formed with evolution of chlorine:

$$\underset{\text{Hypiodous chloride.}}{ICl} + \underset{\text{Potassic chlorate.}}{\left\{\begin{matrix} \mathbf{O}Cl \\ \mathbf{O}Ko \end{matrix}\right.} = \underset{\text{Potassic iodate.}}{\left\{\begin{matrix} \mathbf{O}I \\ \mathbf{O}Ko \end{matrix}\right.} + Cl_2.$$

(See also p. 303.) It forms small, lustrous, regular crystals, soluble in 13 parts of cold water. It decomposes on heating into oxygen and potassic iodide. (*Hyperacid iodates*, p. 303.)

Potassic periodate, $\left\{\begin{matrix} \mathbf{O}I \\ O \\ \mathbf{O}Ko \end{matrix}\right.$, is prepared like the sodium salt (*q.v.*). It forms small rhombic crystals which require 300 times their weight of cold water for solution. Between 250° and 300° C. (482–572° F.) it undergoes decomposition into oxygen and potassic iodate; at a higher temperature it parts with all its oxygen, and is converted into potassic iodide. (For the formulæ of the more complex periodates, see p. 306.)

POTASSIC CARBONATE, $\mathbf{C}OKo_2$, is obtained from the ashes of land plants. Wood ashes, when lixiviated, yield a solution of potassic carbonate, contaminated with small quantities of sodic carbonate, potassic and sodic chlorides, and potassic sulphate. When the solution is evaporated, the impurities crystallize out first, leaving the more soluble potassic carbonate in the mother liquor, from which it may be obtained in the crystallized form by further evaporation. On a large scale it is

prepared from native potassic chloride by a process similar to that by which sodic carbonate is obtained from sodic chloride (see Leblanc's process). Very pure potassic carbonate may be obtained by igniting hydric potassic tartrate (cream of tartar) and extracting with water the mixture of potassic carbonate and carbon (see p. 412). It crystallizes from its aqueous solution in colorless, long, pointed monoclinic prisms of the formula $2\mathbf{C}OKo_2,3\mathbf{O}H_2$. This salt, when dried at 100° C., has the formula $\mathbf{C}OKo_2,\mathbf{O}H$; at a higher temperature it becomes anhydrous. The anhydrous salt is fusible, and, at a bright red heat, volatile. It is deliquescent and very soluble in water, but insoluble in alcohol. The solution has a strong alkaline reaction.—*Hydric potassic carbonate*, $\mathbf{C}OHoKo$, is formed when carbonic anhydride is passed into a concentrated solution of the normal carbonate:

$$\underset{\substack{\text{Potassic}\\\text{carbonate.}}}{\mathbf{C}OKo_2} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{\mathbf{C}O_2} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\substack{\text{Hydric potassic}\\\text{carbonate.}}}{2\mathbf{C}OHoKo.}$$

It crystallizes in anhydrous monoclinic prisms, which are soluble in 3–4 parts of cold water. When the dry salt is heated, or when its aqueous solution is warmed to 80° C. (176° F.), it is decomposed into normal carbonate, carbonic anhydride, and water.

POTASSIC SULPHATE, $\mathbf{S}O_2Ko_2$, is obtained in large quantities as a by-product in many manufacturing processes. It forms anhydrous, colorless, rhombic crystals, with a bitter, saline taste, which are soluble in 10 parts of cold, in 4 parts of boiling water. It decrepitates on heating, and fuses at a bright red heat.—*Hydric potassic sulphate*, $\mathbf{S}O_2HoKo$, is obtained as a by-product in the preparation of nitric acid (p. 215), and may be prepared by heating 1 molecule of the normal salt with 1 molecule of sulphuric acid. From solutions containing an excess of acid, it crystallizes in tabular rhombic crystals. It fuses about 200° C. (392° F.), and may be obtained in monoclinic crystals by the slow solidification of the fused salt. It is readily soluble in water, but an excess of this solvent decomposes it into the normal salt and free sulphuric acid. For this reason, only the normal salt is deposited from dilute solutions. Heated above its fusing-point, it parts with the elements of water and is converted into *potassic pyrosulphate*, $\left\{\begin{array}{l}\mathbf{S}O_2Ko\\ O\\ \mathbf{S}O_2Ko\end{array}\right.$, which, at a temperature of 600° C. (1112° F.), breaks up into normal sulphate and sulphuric anhydride (cf. p. 266).

POTASSIC SULPHITE, $\mathbf{S}OKo_2,2\mathbf{O}H_2$, is prepared by passing sulphurous anhydride into a solution of potassic carbonate until the carbonic anhydride is expelled. It forms monoclinic octahedra, which are very soluble in water and somewhat deliquescent. The solution possesses an alkaline reaction and a bitter taste. When heated, the salt is decomposed, yielding potassic sulphate, potassic sulphide, and potassic hydrate.—*Hydric potassic sulphite*, $\mathbf{S}OHoKo$, is obtained by saturating a concentrated solution of potassic carbonate with sulphurous anhydride. It forms very soluble monoclinic prisms. The addition of alcohol to the

aqueous solution causes the salt to be deposited as a mass of acicular crystals. It has an alkaline reaction and emits an odor of sulphurous anhydride. Exposed to the air in solution, it is gradually oxidized to sulphate.

Potassic pyrosulphite, $\left\{\begin{array}{l}SOKo\\O\\SOKo\end{array}\right.$, is formed when sulphurous anhydride is passed into a warm concentrated solution of potassic carbonate until effervescence ceases and the liquid assumes a greenish tinge. On cooling, it is deposited in granular crystals.

Potassic dithionate, $\left\{\begin{array}{l}SO_2Ko\\SO_2Ko\end{array}\right.$, is prepared by exactly precipitating the barium salt (*q.v.*) with potassic sulphate. It forms hexagonal crystals, soluble in 16 parts of cold, in $1\frac{1}{3}$ parts of boiling water. On heating, it is decomposed into potassic sulphate and sulphurous anhydride.

Potassic thiosulphate, $2SO_2KoKs,3OH_2$.—This is prepared like the sodium salt (*q.v.*). The salt of the above formula is deposited from its aqueous solution at ordinary temperatures, and crystallizes in rhombic octahedra. At temperatures above 30° C. (86° F.), the solution deposits thin four-sided prisms of the formula $3SO_2KoKs,OH_2$. At 200° C. (392° F.) the water of crystallization is expelled, and at a still higher temperature the salt is decomposed into a mixture of potassic sulphate and pentasulphide:

$$\underset{\text{Potassic thiosulphate.}}{4SO_2KoKs} = \underset{\text{Potassic sulphate.}}{3SO_2Ko_2} + \underset{\text{Potassic pentasulphide.}}{K_2S_5}.$$

Potassic selenate, SeO_2Ko_2, is prepared by fusing selenious anhydride with nitre, extracting with water, and evaporating. It crystallizes in forms exactly resembling those of potassic sulphate. It may be distinguished from this salt by evolving chlorine when heated with hydrochloric acid, at the same time undergoing reduction to potassic selenite. The *selenite,* $SeOKo_2$, forms granular, very soluble deliquescent crystals.

Potassic tellurate, TeO_2Ko_2. *Hydric potassic tellurate,* $2TeO_2HoKo,3OH_2$. These salts are obtained by adding the requisite quantities of telluric acid to solutions of potassic carbonate. The neutral salt is very soluble, the acid salt sparingly soluble, in cold water. Other more complex tellurates of potassium are known (see pp. 289, 290).

POTASSIC PHOSPHATES.—a. *Potassic orthophosphate,* $POKo_3$, is prepared by igniting 2 molecules of phosphoric anhydride with 3 molecules of potassic carbonate, dissolving in water and evaporating. It forms colorless, very soluble needles.—*Hydric dipotassic orthophosphate,* $POHoKo_2$, may be obtained in solution by adding potassic carbonate to a solution of phosphoric acid till a slight alkaline reaction is produced. It is uncrystallizable.—*Dihydric potassic orthophosphate,* $POHo_2Ko$, is prepared by adding phosphoric acid to a solution of potassic carbonate till the liquid has a strongly acid reaction. On evaporating, large colorless quadratic crystals, very soluble in water, are obtained.

b. *Potassic pyrophosphate,* $\left\{\begin{array}{l}POKo_2\\O\\POKo_2\end{array}\right.,3OH_2$, is prepared by igniting hydric dipotassic phosphate (cf. p. 355). It may also be obtained by almost neutralizing a solution of phosphoric acid with alcoholic potash, then adding alcohol as long as milkiness is produced, and separating, drying and igniting the syrupy precipitate. The mass is extracted with water and evaporated to the point of crystallization. It forms a radio-crystalline mass, very soluble in water. One molecule of water of crystallization is driven off at 100° C., but a temperature of 300° C. (572° F.) is required to render the salt anhydrous. In the

anhydrous state it is deliquescent.—*Dihydric dipotassic pyrophosphate*, $P_2O_3Ho_2Ko_2$, is obtained by precipitating with alcohol the solution of the neutral salt in acetic acid. The syrupy mass is washed with alcohol to remove the potassic acetate and dried over sulphuric acid. It forms a white deliquescent mass.

c. *Potassic metaphosphate*, PO_2Ko, is prepared by igniting dihydric potassic phosphate (cf. p. 354). It is thus obtained as a translucent mass, almost insoluble in water, readily soluble in dilute acids. Metaphosphates of complex constitution are also known (p. 354).

Potassic phosphite, $PHoKo_2$.—This salt is obtained by neutralizing the aqueous acid with potassic hydrate or carbonate and evaporating *in vacuo*. It is deliquescent and very soluble, and can only with difficulty be obtained in a crystalline form.

Potassic arsenates.—These are prepared like the corresponding phosphates, with which they are isomorphous, and which they closely resemble in their other properties. *Potassic arsenate*, $AsOKo_3$, forms deliquescent needles; *hydric dipotassic arsenate*, $AsOHoKo_2$, is uncrystallizable and deliquescent; *dihydric potassic arsenate*, $AsOHo_2Ko$, which is most readily obtained by fusing arsenious acid with nitre, extracting with water and evaporating, forms large soluble quadratic crystals.

Very little is known concerning the *arsenites* of potassium.

Potassic antimonates.—When a mixture of 1 part of powdered antimony with 4 parts of nitre is deflagrated, and the mass extracted with tepid water, *potassic metantimonate*, SbO_2Ko, remains as a white powder, almost insoluble in cold water. When this substance is boiled with water it gradually dissolves, taking up the elements of water and forming *dihydric potassic antimonate*, which, on evaporating the solution to a syrup, separates out in granular crystals of the formula $2SbOHo_2Ko,3OH_2$. By fusing antimonic acid or either of the above antimonates with a large excess of potash, dissolving the mass in water and evaporating, warty crystals of *tetrapotassic pyrantimonate*, $Sb_2O_3Ko_4$, are obtained. This salt is stable in solution only in presence of an excess of caustic potash; pure water decomposes it into free potash and *dihydric dipotassic pyrantimonate* (*metantimonate* of Fremy), $Sb_2O_3Ho_2Ko_2,6OH_2$, a granular, almost insoluble powder, which is converted by long boiling with water into soluble dihydric potassic antimonate (see above.)

Potassic borate.—The *metaborate*, $BOKo$, is prepared by fusing together equal molecules of boric anhydride and potassic carbonate. It is very soluble, and crytallizes with difficulty. Exposed to the air in solution, it absorbs carbonic anhydride and is converted into *hydric potassic diborate*, $B_2O_2HoKo,2OH_2$. A *dipotassic tetraborate*, $B_4O_5Ko_2,6OH_2$, is obtained by mixing hot concentrated solutions of 1 molecule of potassic carbonate and 2 molecules of boric anhydride, and cooling to 6° C. (42.8° F.). The salt crystallizes in hard, transparent, prismatic crystals, with a vitreous lustre. When a boiling solution of potassic carbonate is acidified with boric acid, it deposits on cooling prismatic crystals of *hydric potassic hexaborate*, $B_6O_8HoKo,4OH_2$.

Potassic silicate is formed when silicic acid or amorphous silicic anhydride is dissolved in potassic hydrate. It is generally prepared by fusing together potassic carbonate and white quartz sand. No compound of definite composition is known. Potassic silicate, under the name of *soluble glass*, is employed as a cement.

COMPOUNDS OF POTASSIUM WITH SULPHUR.

The following have been obtained:

Dipotassic sulphide, ...	SK_2.	K—S—K
Dipotassic disulphide, . .	K_2S_2.	K—S—S—K
Dipotassic trisulphide, . . .	K_2S_3.	K—S—S—S—K
Dipotassic tetrasulphide, .	K_2S_4.	K—S—S—S—S—K
Dipotassic pentasulphide, .	K_2S_5.	K—S—S—S—S—S—K
Dipotassic heptasulphide, .	K_2S_7 ?	K—S—S—S—S—S—S—S—K

DIPOTASSIC SULPHIDE, $\mathbf{S}K_2$, is formed when potassic sulphate is reduced by ignition with carbon or in a current of hydrogen:

$$\underset{\text{Potassic sulphate.}}{\mathbf{S}O_2Ko_2} + 4H_2 = \underset{\text{Dipotassic sulphide.}}{\mathbf{S}K_2} + \underset{\text{Water.}}{4\mathbf{O}H_2}.$$

It is a reddish crystalline mass, which deliquesces when exposed to the air.

A solution of dipotassic sulphide may be obtained by dividing a concentrated aqueous solution of potassic hydrate into two equal parts, saturating one part with sulphuretted hydrogen so as to form potassic sulphhydrate (*q.v.*), and then adding the other part:

$$\underset{\text{Potassic hydrate.}}{KHo} + \underset{\text{Potassic sulphhydrate.}}{KHs} = \underset{\text{Dipotassic sulphide.}}{\mathbf{S}K_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

The concentrated solution deposits deliquescent prismatic or tabular crystals of the formula $\mathbf{S}K_2,5\mathbf{O}H_2$.

Dipotassic disulphide, K_2S_2, is formed when the sulphhydrate is oxidized by exposure to air:

$$\underset{\text{Potassic sulphhydrate.}}{2KHs} + O = \underset{\text{Dipotassic disulphide.}}{K_2S_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

By evaporation *in vacuo* the disulphide is obtained as an orange-colored mass.

The other polysulphides of potassium are prepared by fusing dipotassic sulphide with sulphur. Below 600° C. (1112° F.) the *pentasulphide* is formed; between 600° and 800° C. (1112–1472° F.) the *tetrasulphide;* and at 900° C. (1652° F.) the *trisulphide.* They are brownish-yellow solids with an alkalide reaction. Exposed to moist air they emit an odor of sulphuretted hydrogen.

Solutions of these polysulphides are formed when solutions of dipotassic sulphide are boiled with the requisite quantities of flowers of sulphur. In this way crystallized aquates of some of these sulphides may be obtained, for example $K_2S_4,2\mathbf{O}H_2$, which forms orange-colored laminæ.

COMPOUND OF POTASSIUM WITH HYDROSULPHYL.

POTASSIC SULPHHYDRATE, KHs, is obtained by heating potassium in a current of sulphuretted hydrogen:

$$\underset{\text{Sulphuretted hydrogen.}}{2\mathbf{S}H_2} + K_2 = \underset{\text{Potassic sulphhydrate.}}{2\mathbf{S}KH} + H_2,$$

or by passing sulphuretted hydrogen over potassic carbonate heated to low redness:

$$\underset{\text{Potassic carbonate.}}{\mathbf{C}OKo_2} + \underset{\text{Sulphuretted hydrogen.}}{2\mathbf{S}H_2} = \underset{\text{Potassic sulphhydrate.}}{2\mathbf{S}KH} + \underset{\text{Carbonic anhydride.}}{\mathbf{C}O_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

It forms a flesh-colored crystalline mass, which melts at low redness to a yellow liquid.

A solution of potassic sulphhydrate may be obtained by saturating an aqueous solution of potassic hydrate with sulphuretted hydrogen:

KHo	$+$	$\mathbf{S}H_2$	$=$	KHs	$+$	$\mathbf{O}H_2.$
Potassic hydrate.		Sulphuretted hydrogen.		Potassic sulphhydrate.		Water.

The solution, when concentrated *in vacuo*, deposits colorless rhombohedra of the formula $2KHs,\mathbf{O}H_2$.

Reactions of potassic sulphhydrate, dipotassic sulphide and the higher potassic sulphides.—1. Potassic sulphhydrate and dipotassic sulphide, when acted upon by acids, yield sulphuretted hydrogen:

KHs	$+$	HCl	$=$	KCl	$+$	$\mathbf{S}H_2.$
Potassic sulphhydrate.		Hydrochloric acid.		Potassic chloride.		Sulphuretted hydrogen.

$\mathbf{S}K_2$	$+$	$2HCl$	$=$	$2KCl$	$+$	$\mathbf{S}H_2.$
Dipotassic sulphide.		Hydrochloric acid.		Potassic chloride.		Sulphuretted hydrogen.

2. The higher sulphides, when similarly treated, yield sulphuretted hydrogen with precipitation of sulphur:

K_2S_3	$+$	$2HCl$	$=$	$2KCl$	$+$	$\mathbf{S}H_2$	$+$	$S_2.$
Dipotassic trisulphide.		Hydrochloric acid.		Potassic chloride.		Sulphuretted hydrogen.		

3. When dipotassic sulphide is exposed in aqueous solution to the action of the air, it absorbs oxygen and is converted into a mixture of potassic thiosulphate and potassic hydrate:

$2\mathbf{S}K_2$	$+$	$\mathbf{O}H_2$	$+$	$2O_2$	$=$	$\mathbf{S}O_2KoKs$	$+$	$2KHo.$
Dipotassic sulphide.		Water.				Potassic thiosulphate.		Potassic hydrate.

4. A mixture of the higher potassic sulphides with potassic thiosulphate, known under the name of *hepar sulphuris* or *liver of sulphur*, may be obtained as a brown mass by heating potassic carbonate with sulphur:

$3\mathbf{C}OKo_2$	$+$	$4S_2$	$=$	$2K_2S_3$	$+$	$\mathbf{S}O_2KoKs$	$+$	$3\mathbf{C}O_2.$
Potassic carbonate.				Dipotassic trisulphide.		Potassic thiosulphate.		Carbonic anhydride.

$3\mathbf{C}OKo_2$	$+$	$6S_2$	$=$	$2K_2S_5$	$+$	$\mathbf{S}O_2KoKs$	$+$	$3\mathbf{C}O_2.$
Potassic carbonate.				Dipotassic pentasulphide.		Potassic thiosulphate.		Carbonic anhydride.

5. The last mixture, when acted upon by acids, undergoes successively the following decomposition:

$$2K_2S_5 + SO_2KoKs + 6HCl = 6KCl + SO_2HoHs + 2SH_2 + 4S_2;$$

Dipotassic pentasulphide.	Potassic thiosulphate.	Hydrochloric acid.	Potassic chloride.	Thiosulphuric acid.	Sulphuretted hydrogen.

then—

$$SO_2HoHs = SO_2 + S + OH_2;$$

Thiosulphuric acid.	Sulphurous anhydride.	Water.

and finally—

$$5SH_2 + 5SO_2 = \begin{cases} SO_2Ho \\ S''_3 \\ SO_2Ho \end{cases} + 4OH_2 + 5S.$$

Sulphuretted hydrogen.	Sulphurous anhydride.	Pentathionic acid.	Water.

SULPHO-SALTS OF POTASSIUM.

Potassic sulpharsenate, $AsS''Ks_3$, is prepared by dissolving arsenic sulphide, or arsenious sulphide together with sulphur, in a solution of potassic sulphide or potassic sulphhydrate:

$$As_2S''_5 + 3SK_2 = 2AsS''Ks_3.$$

Arsenic sulphide.	Potassic sulphide.	Tripotassic sulpharsenate.

$$As_2S''_3 + 3SK_2 + S_2 = AsS''Ks_3.$$

Arsenious sulphide.	Potassic sulphide.	Tripotassic sulpharsenate.

It is also formed when a solution of tripotassic arsenate is saturated with sulphuretted hydrogen:

$$AsOKo_3 + 3SH_2 = AsS''Ks_3 + 3OH_2.$$

Tripotassic arsenate.	Sulphuretted hydrogen.	Tripotassic sulpharsenate.	Water.

It is obtained as a deliquescent crystalline mass of the formula $AsS''Ks_3,OH_2$ (perhaps $AsHoHsKs_3$).

Potassic sulphantimonate, $SbS''Ks_3$, may be obtained in the same manner as the sulpharsenate, employing the corresponding sulphides of antimony. In practice, it is prepared by heating together finely powdered antimonious sulphide, sulphur, potassic carbonate, slaked lime and water, filtering and evaporating. It forms yellow deliquescent crystals of the formula $2SbS''Ks_3,9OH_2$.

Treated with dilute acids in the cold, the alkaline sulpharsenates and sulphantimonates yield the corresponding acids $AsS''Hs_3$ and $SbS''Hs_3$. On boiling the solutions these acids are decomposed into arsenic and antimonic sulphides respectively, and sulphuretted hydrogen:

$$2AsS''Hs_3 = As_2S''_5 + 3SH_2.$$

Sulpharsenic acid.	Arsenic sulphide.	Sulphuretted hydrogen.

COMPOUND OF POTASSIUM WITH NITROGEN AND HYDROGEN.

Potassic amide, NKH_2, is obtained by heating potassium gently in a current of dry gaseous ammonia. The potassium fuses in the gas to a blue liquid, which solidifies on cooling to a flesh-colored mass. Water decomposes it with violence into ammonia and potassic hydrate:

$$\underset{\text{Potassic amide.}}{NKH_2} + \underset{\text{Water.}}{OH_2} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Potassic hydrate.}}{OKH.}$$

When strongly heated in an atmosphere free from oxygen, it is decomposed into ammonia and potassic nitride:

$$\underset{\text{Potassic amide.}}{3NKH_2} = \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Potassic nitride.}}{NK_3.}$$

Potassic nitride is a greenish-black substance which, in contact with air, spontaneously inflames.

General Properties and Reactions of the Compounds of Potassium.—The salts of potassium with colorless acids are colorless. *Platinic chloride* precipitates from hydrochloric acid solutions of potash salts a yellow crystalline powder of potassic platinic chloride ($PtCl_4$,$2KCl$), very sparingly soluble in water, insoluble in alcohol and ether; this salt, when heated to redness, is decomposed with evolution of chlorine, leaving potassic chloride and metallic platinum. *Hydrofluosilicic acid* gives a gelatinous precipitate of potassic silicofluoride, SiK_2F_6. *Tartaric acid* in excess precipitates from moderately concentrated solutions hydric potassic tartrate, $\left\{\begin{matrix} CHHo(COKo) \\ CHHo(COHo), \end{matrix}\right.$ as a white crystalline powder. The compounds of potassium impart to a non-luminous flame a violet coloration which, when viewed through blue cobalt glass or a solution of indigo, appears red. The spectrum of potassium contains two characteristic lines—$K\alpha$ in the red and $K\beta$ in the violet—both coincident with lines of the solar spectrum.

SODIUM, Na_2?

Atomic weight = 23. *Probable molecular weight* = 46. *Sp. gr.* 0.97. *Fuses at* 95.6° C. (172° F.). *Boils at a red heat. Atomicity* ′. *Evidence of atomicity:*

Sodic chloride, ...	$NaCl$.
Sodic hydrate, ...	$ONaH$.
Sodic oxide, ...	ONa_2.

History.—Metallic sodium was first obtained by Davy, in 1807, by the electrolysis of sodic hydrate.

Occurrence.—Sodium is an abundant and widely distributed element. It does not occur in the free state. In combination with silicic acid it is found in many minerals and rocks, and in soils. As nitrate, or Chili saltpetre, it forms large beds on the surface of the ground in dry districts in Chili and Peru. As carbonate and as iodide it occurs in the ashes of sea plants. The chloride is, however, the form in which it is found in the greatest abundance—thus, as rock salt, in sea water, and in the water of salt springs. The borate and sulphate also occur in nature.

Preparation.—1. Davy obtained sodium by electrolyzing, between

the poles of a powerful battery, solid sodic hydrate moistened with water (see Potassium, p. 411):

$$2ONaH = Na_2 + H_2 + O_2.$$

2. Sodium is also liberated from the hydrate by acting upon it with metallic iron at a strong white heat. The reaction is the same as in the case of potassium (p. 412).

3. On a manufacturing scale, sodium is prepared by distilling from a cylindrical iron retort a mixture of dry sodic carbonate and charcoal, to which a small quantity of chalk is added to prevent the fusion of the mass and the consequent separation of the charcoal:

$$\underset{\text{Sodic carbonate.}}{CONao_2} + 2C = Na_2 + \underset{\text{Carbonic oxide.}}{3CO}.$$

Properties.—Sodium resembles potassium in its properties. It is a lustrous, silver-white metal, which almost instantaneously tarnishes from oxidation when exposed to the air. At a temperature of —20° C. (—4° F.) it is hard, but at ordinary temperatures it is of the consistence of wax. When heated in air it burns with a yellow flame, forming oxides of sodium. By fusing it in a tube filled with coal-gas, allowing it partially to solidify, and pouring off the still liquid portion, it may be obtained in crystals.

Reactions.—The reactions of sodium are similar to those of potassium, but less energetic. Thus, sodium decomposes water with evolution of hydrogen, the metal moving rapidly on the surface with a hissing noise, but the heat developed is not sufficient to inflame the hydrogen. If, however, the water be previously heated above 60° C. (140° F.), or if, by rendering the water viscid with glue, or by placing the metal on wet blotting paper, the sodium be prevented from moving, and therefore from too rapidly cooling, the hydrogen will inflame. Under these circumstances, the reaction is, however, sometimes attended with a violent explosion. Sodium is not acted upon by dry chlorine or bromine, even when gently heated with these reagents; in presence of moisture, however, chloride and bromide of sodium are formed.

Uses.—Sodium, like potassium, is employed in the preparation of various metals and metalloids from their oxides or chlorides. It acts by combining with the oxygen or chlorine, and liberating the element which it is desired to isolate. On account of its greater cheapness and lower atomic weight, it is generally preferred for this purpose to potassium (see p. 413). It is thus used in the arts, in the preparation of aluminium and magnesium from their chlorides. In the laboratory it is also employed as a source of nascent hydrogen. The substance to be submitted to the hydrogenating action is brought, along with water or alcohol, in contact with the sodium (preferably in the form of an amalgam, or alloy of the metal with mercury—the mercury being added in order to moderate the violence of the reaction), and in this way the hydrogen from the water or alcohol, instead of being liberated, combines with the substance.

COMPOUND OF SODIUM WITH HYDROGEN.

Sodic hydride, Na_4H_2. Sodium when heated to a temperature between 300° and 420° C. (572°–788° F.) in a current of dry hydrogen, absorbs the gas with formation of sodic hydride, a silvery metallic mass of sp. gr. 0.959, which is soft at ordinary temperatures, but at lower temperatures brittle. It fuses at a somewhat lower temperature than sodium. It is more permanent in air than the corresponding potassium compound. It begins to dissociate under ordinary pressures at 420° C. (788° F.); *in vacuo,* at 300° C. (572° F.).

COMPOUNDS OF SODIUM WITH THE HALOGENS.

Sodic chloride (*Common salt*), NaCl.—This important compound occurs in sea-water (2.5 to 3 per cent.), in salt springs, and as rock salt. The most celebrated salt mines are those of Wieliczka, in Galicia, in which the salt deposit is 500 miles long, 20 miles broad, and 1200 feet thick. When the salt is pure, as is sometimes the case with rock salt, it is obtained direct by ordinary mining operations. Generally, however, it is contaminated with earthy matters, from which it must be freed by dissolving in water and recrystallizing. Salt is also obtained from sea-water: in warm climates, by allowing the water to evaporate in shallow basins; in cold climates, by letting it freeze and removing the ice, the salt remaining in the liquid. Chloride of sodium is formed when sodium is burnt in chlorine. It crystallizes in large colorless anhydrous cubes belonging to the regular system; from solutions containing urea it is deposited in octahedra. Below —10° C. it crystallizes from water in monoclinic plates of the formula $NaCl,2\mathbf{O}H_2$, which at ordinary temperatures part with their water of crystallization and fall to pieces, being converted into a number of minute cubes. It is almost equally soluble in hot and cold water: at 0° C. water takes up 36 parts, at 100° C. 39 parts. Alcohol does not dissolve it. At a red heat it is fusible and volatile.

Sodic bromide, NaBr, is prepared by neutralizing hydrobromic acid with sodic carbonate, or by decomposing ferrous bromide ($\mathbf{Fe}Br_2$) with a solution of sodic carbonate (see Potassic iodide, p. 414). It crystallizes from its aqueous solution above 30° C. in anhydrous cubes; below this temperature in monoclinic prisms of the formula $NaBr,2\mathbf{O}H_2$. It is readily soluble both in water and in alcohol.

Sodic iodide, NaI, is prepared like the bromide, which it also resembles in its crystallographical characteristics. Above 20° C. it crystallizes from water in anhydrous cubes; at lower temperatures in monoclinic forms with 2 molecules of water of crystallization. Both water and alcohol dissolve it freely. Like potassic iodide it forms double compounds with the iodides of the heavy metals.

Sodic fluoride, NaF, is obtained by neutralizing hydrofluoric acid with sodic carbonate. It crystallizes in anhydrous cubes, which are soluble in 25 parts of cold, very slightly more soluble in boiling water. It forms numerous double compounds with other fluorides and with hydrofluoric acid. The mineral *cryolite* is an aluminio-sodic fluoride of the formula $\mathbf{Al}_2F_6,6NaF$. *Sodic silicofluoride,* SiF_6Na_2 ($=\mathbf{Si}F_4,2NaF$), forms small lustrous hexagonal crystals, sparingly soluble in water.

COMPOUNDS OF SODIUM WITH OXYGEN AND HYDROXYL.

SODIC OXIDE, $\mathbf{O}Na_2$.—When sodium burns in air a mixture of sodic oxide with disodic dioxide (Na_2O_2) is formed. By heating this mixture to a very high temperature, the dioxide parts with half its oxygen, and is converted into sodic oxide, which is thus obtained as a gray mass with a conchoidal fracture. Water converts it, with evolution of great heat, into the hydrate.

Disodic dioxide, $\left\{\begin{matrix}\mathbf{O}Na\\ \mathbf{O}Na\end{matrix}\right.$, is obtained by heating sodium in oxygen gas till the weight becomes constant. It is a white substance, which becomes yellow on heating, but turns white again on cooling. In contact with water, it evolves great heat, and parts with some of its oxygen.

SODIC HYDRATE (*Caustic soda*), NaHo.—This compound is formed by the action of water upon sodium or upon sodic oxide. It is prepared by acting upon a boiling solution of sodic carbonate with milk of lime:

$$\underset{\text{Sodic carbonate.}}{\mathbf{C}ONao_2} + \underset{\text{Calcic hydrate.}}{\mathbf{Ca}Ho_2} = \underset{\text{Sodic hydrate.}}{2NaHo} + \underset{\text{Calcic carbonate.}}{\mathbf{C}OCao''}.$$

The solution of sodic hydrate is decanted from the insoluble calcic carbonate and concentrated, first in an iron and lastly in a silver basin. Most of the sodic hydrate of commerce is obtained in the manufacture of sodic carbonate (see Leblanc's process), the calcic oxide, which is formed in roasting the *black ash*, acting upon a portion of the sodic carbonate when the mass is treated with water. The caustic soda remains in the mother liquors after the separation of the other salts—carbonate and sulphate. A small quantity of sodic nitrate is added in order to oxidize the sodic sulphide to sulphate.—Sodic hydrate is an opaque white fibrous substance of sp. gr. 2.00, resembling potassic hydrate in nearly all its properties. It fuses below redness, and at a higher temperature volatilizes. When exposed to the air in large masses, it does not deliquesce, but merely becomes moist on the surface, after which a coating of the non-deliquescent carbonate is formed, which protects it from further action. It is very soluble, both in water and in alcohol, yielding powerfully caustic solutions. The concentrated aqueous solution, when exposed to a low temperature, deposits crystals of the formula $2NaHo,7\mathbf{O}H_2$, which fuse at 6° C. (43° F.) to a liquid of sp. gr. 1.405. Its solutions absorb carbonic anhydride from the air. With acids it yields the corresponding sodium salts:

$$\underset{\text{Sodic hydrate.}}{NaHo} + \underset{\text{Nitric acid.}}{\mathbf{N}O_2Ho} = \underset{\text{Sodic nitrate.}}{\mathbf{N}O_2Nao} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

OXY-SALTS OF SODIUM.

SODIC NITRATE (*Chili saltpetre*), $\mathbf{N}O_2Nao$, occurs, more or less contaminated with other salts, in enormous deposits in Chili and Peru. It can be readily purified by crystallization, and forms rhombohedral

crystals fusing at 313° C. (595° F.). It is soluble in about its own weight of water. Owing to its slightly deliquescent character, it cannot be used in the manufacture of ordinary gunpowder, but it has been employed in the case of powders in which extreme rapidity of combustion is not essential. In other respects it resembles potassic nitrate. It is used in the preparation of "converted nitre" (p. 416), and nitric acid, and also as a manure.

Sodic nitrite, $\mathbf{N}ONao$, is prepared like the potassium salt (p. 416). It forms colorless rhombohedra, and is less deliquescent than the potassium salt. It is soluble in alcohol.

Sodic chlorate, $\left\{\begin{matrix}\mathbf{O}Cl\\ \mathbf{O}Nao\end{matrix}\right.$, is formed in the same manner as the potassium salt (p. 182), but, owing to its solubility and the impossibility of separating it from the chloride which is formed simultaneously, cannot be so prepared. It is most readily obtained by neutralizing a solution of chloric acid with sodic carbonate and evaporating. It forms large transparent crystals belonging to the regular system, and exhibiting hemihedral faces, which in some crystals are positive, in others negative. These crystals possess a corresponding action on the ray of polarized light, the positive crystals being dextrorotatory, the negative lævorotatory. It is soluble in its own weight of water at ordinary temperatures, and in half its weight at 100° C. In other respects it resembles the potassium salt.

Sodic perchlorate, $\left\{\begin{matrix}\mathbf{O}Cl\\ O\\ \mathbf{O}Nao\end{matrix}\right.$, is prepared by neutralizing perchloric acid with sodic hydrate or carbonate. It is a deliquescent salt, readily soluble in water, soluble also in alcohol.

Sodic bromate, $\left\{\begin{matrix}\mathbf{O}Br\\ \mathbf{O}Nao\end{matrix}\right.$, is prepared like the potassium salt (p. 417). It forms small lustrous crystals, soluble in about 3 parts of water at ordinary temperatures. Below —4° C. (25° F.) it crystallizes in four-sided prisms containing water of crystallization.

Sodic iodate, $\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Nao\end{matrix}\right.$, is obtained in the same manner as the potassium salt (p. 417). It crystallizes at ordinary temperatures with one molecule of water of crystallization in silky needles. It is soluble in 11–12 parts of water. Below 5° C. (41° F.) it is deposited in transparent rhombic prisms with 5 molecules of water of crystallization. It forms well-crystallized double salts with the chloride, bromide, and iodide of sodium. The compound with sodic chloride has the formula

$$2\left\{\begin{matrix}\mathbf{O}I\\ \mathbf{O}Nao\end{matrix}\right.,3NaCl,9\mathbf{O}H_2.$$

Sodic periodate, $\left\{\begin{matrix}\mathbf{O}I\\ O\\ \mathbf{O}Nao\end{matrix}\right.,3\mathbf{O}H_2$. When chlorine is passed into a solution of sodic iodate in caustic soda, a sparingly soluble basic salt of the formula $IO_5HNa_2,\mathbf{O}H_2$ is deposited, which, when dissolved in dilute nitric acid and evaporated, is converted into the normal salt $IO_3Nao,3\mathbf{O}H_2$. (On the formulation of the periodates, see p. 305.) The normal salt forms colorless hexagonal crystals, soluble in 12 parts of water at ordinary temperatures. The crystals part with their water of crystallization at 100° C. Heated to 275° C. (527° F.) the anhydrous salt gives off oxygen, and is converted into iodate.

Sodic carbonate, $\mathbf{C}ONao_2$, occurs in the soda lakes of Egypt and Hungary, and in the volcanic springs of Iceland. It constitutes the greater part of the ash of sea plants, from which source it was formerly obtained. The two methods at present employed in its preparation are: the *process of Leblanc* and the *ammonia-soda process*, both of which start from sodic chloride.

1. *Leblanc's Process.*—This process consists of two parts: the conversion of the sodic chloride into sodic sulphate or salt cake, known as the *salt-cake process;* and the manufacture of sodic carbonate or soda

ash from the sulphate, known as the *soda-ash process.* In the first of these processes the sodic chloride is treated, in a large hemispherical cast-iron pan heated over a furnace, with the requisite quantity of sulphuric acid. The hydrochloric acid which is evolved passes through towers filled with coke, over which a stream of water trickles, and is thus absorbed. After heating for some time, the mixture of acid and salt solidifies, upon which it is transferred from the iron pan to the bed of a reverberatory furnace, where the decomposition is completed.

In the soda-ash processs, the sodic sulphate or salt cake, as it is technically termed, is mixed with crushed chalk or limestone and small coal, and gradually heated in a reverberatory furnace. The action takes place in the two following stages:

$$\underset{\text{Sodic sulphate.}}{SO_2Nao_2} + 4C = \underset{\text{Sodic sulphide.}}{SNa_2} + \underset{\text{Carbonic oxide,}}{4CO,}$$

and

$$\underset{\text{Sodic sulphide.}}{SNa_2} + \underset{\text{Calcic carbonate.}}{COCao''} = \underset{\text{Sodic carbonate.}}{CONao_2} + \underset{\text{Calcic sulphide,}}{CaS'',}$$

the calcic sulphide combining with the excess of calcic oxide (formed from the chalk), and yielding insoluble calcic oxysulphide.

These reactions take place simultaneously in the above operation. When the change is complete, the mass, which is known as *black ash,* is allowed to cool, and is then extracted with water, which dissolves the sodic carbonate, leaving behind the insoluble oxysulphide. On evaporating, the sodic carbonate crystallizes out, and may be purified by recrystallization.

A portion of the chalk is converted by the heat into quicklime, and this gives rise to the formation of sodic hydrate when the mass is treated with water. This sodic hydrate may be recovered from the mother liquors of the carbonate (p. 427).

2. *Ammonia-soda Process.*—By the action of hydric ammonic carbonate on a concentrated solution of sodic chloride, hydric sodic carbonate and ammonic chloride are produced:

$$\underset{\text{Hydric ammonic carbonate.}}{COHo(N^vH_4O)} + \underset{\text{Sodic chloride.}}{NaCl} = \underset{\text{Hydric sodic carbonate.}}{COHoNao} + \underset{\text{Ammonic chloride.}}{NH_4Cl.}$$

The sparingly soluble hydric sodic carbonate separates out, whilst the ammonic chloride remains in solution. By heating the hydric sodic carbonate, it is converted, with evolution of carbonic anhydride, into the normal salt:

$$\underset{\text{Hydric sodic carbonate.}}{2COHoNao} = \underset{\text{Sodic carbonate.}}{CONao_2} + \underset{\text{Carbonic anhydride.}}{CO_2} + \underset{\text{Water.}}{OH_2.}$$

The carbonic anhydride is employed in reconverting into hydric ammonic carbonate, the ammonia recovered from the ammonic chloride.

Sodic carbonate crystallizes at ordinary temperatures in efflorescent monoclinic crystals of the formula $CONao_2,10OH_2$, fusing at 50° C. (122° F.) to a clear liquid, which gives off water, and deposits a pulverulent salt, with one molecule of water of crystallization. At temperatures between 30° and 50° C. (86–122° F.) it is deposited in rhombic crystals with $7OH_2$. It is readily soluble in water, with a maximum solubility at 38° C. (100° F.).

100 parts of water dissolve:

At 0° C. (32° F.), . .	7 parts of anhydrous salt.
At 15° C. (59° F.), . .	16 parts of anhydrous salt.
At 38° C. (100° F.), . .	51 parts of anhydrous salt.
At 104° C. (219° F.), . .	45 parts of anhydrous salt.

Anhydrous sodic carbonate fuses at a bright red heat, and may be volatilized at a white heat. The chief consumption of sodic carbonate is in the manufacture of glass, in soap-making, and in bleaching calico.

Hydric sodic carbonate, $COHoNao$, occurs naturally in many mineral waters. It is formed when a concentrated solution of the normal carbonate is saturated with carbonic anhydride. The crystallized normal carbonate also absorbs carbonic anhydride with evolution of heat, a property which is taken advantage of in the preparation of the salt on a large scale. The acid carbonate can be readily separated from the normal carbonate by its more sparing solubility. Hydric sodic carbonate is also obtained in the preparation of sodic carbonate by the ammonia-soda process (p. 429). It forms monoclinic prisms, soluble in 10–11 parts of water at ordinary temperatures. When its solution is heated, the salt parts with a portion of its carbonic acid, yielding the so-called sesquicarbonate, $CONao_2,2COHoNao,2OH_2$, which may be obtained in crystals by cooling the solution. The sesquicarbonate also occurs in large deposits in Africa and South America, the natural product being known as *trona* or *urao*. If the solution of hydric sodic carbonate be boiled for a sufficient length of time, it is entirely decomposed into normal carbonate, carbonic anhydride, and water. The same decomposition takes place when the dry salt is heated.

Potassic sodic carbonate, $COKoNao,6OH_2$.—This salt crystallizes from the solution of a mixture of potassic and sodic carbonates. It forms efflorescent monoclinic crystals. It cannot be recrystallized from water without decomposition. The anhydrous salt fuses at a red heat more readily than either potassic or sodic carbonate. On account of this property it is employed in mineral analysis for the decomposition of silicates by fusion.

SODIC SULPHATE (*Glauber's salt*), SO_2Nao_2, occurs in nature in the anhydrous form as the mineral *thenardite*, and with ten molecules of water of crystallization as *Glauber's salt*. *Glauberite* is a native sodic calcic sulphate of the formula $\begin{matrix}SO_2Nao\\SO_2Nao\end{matrix}Cao''$. Sodic sulphate often occurs in sea-water and in the water of brine springs. It is prepared in enormous quantities under the name of *salt cake* as a preliminary step in the manufacture of sodic carbonate by Leblanc's process (p. 429).

It crystallizes at ordinary temperatures in large colorless efflorescent monoclinic prisms of the formula $\mathbf{S}O_2Nao_2,10\mathbf{O}H_2$, which fuse at 33° C. in their water of crystallization. It is very soluble in water, with a maximum solubility at 33° C.

100 parts of water dissolve:

At 0° C., ...	5	parts of anhydrous salt.
At 20° C., ...	20	parts of anhydrous salt.
At 33° C., ...	50.6	parts of anhydrous salt.
At 103° C., ...	42.65	parts of anhydrous salt.

(See also p. 127). A solution saturated at 33° C. deposits, when heated above this temperature, small rhombic octahedra of the formula $\mathbf{S}O_2Nao_2,\mathbf{O}H_2$ (formerly supposed to be anhydrous; see, however, Thompson, *Ber. d. deutsch. chem. Ges.*, 11, 2042). This monaquate is always deposited from solutions at temperatures above 40° C. (104° F.). When a solution, saturated at 33° C. (91° F.) is cooled, it does not, if protected from the air, deposit crystals, and in hermetically sealed vessels, may be preserved for an indefinite period in this supersaturated condition; but the introduction of a fragment of the solid salt, or even contact with dust from the air, which probably always contains the solid salt, is sufficient to determine the solidification of the liquid to a magma of crystals, this process being accompanied by a rise of temperature. When the supersaturated solution is evaporated *in vacuo* over sulphuric acid, it deposits crystals of a salt having the formula $\mathbf{S}O_2Nao_2,7\mathbf{O}H_2$, this probably being the form in which the substance is present in the supersaturated solution. Crystallized sodic sulphate dissolves in concentrated hydrochloric acid with great absorption of heat. A useful freezing mixture is obtained by pouring 5 parts of the acid upon 8 of the sulphate.—*Hydric sodic sulphate*, $\mathbf{S}O_2HoNao$, is prepared like the potash salt (p. 418). It crystallizes at ordinary temperatures in monoclinic prisms with 1 aq.;* above 50° C., in anhydrous triclinic forms. It is readily fusible. Heated above its fusing point it parts with the elements of water, yielding sodic pyrosulphate, $\mathbf{S}_2O_5Nao_2$; at a still higher temperature sulphuric anhydride is expelled and the normal sulphate remains.

Tripotassic sodic disulphate, $\mathbf{S}O_2Ko_2,\mathbf{S}O_2KoNao$, is obtained in hexagonal plates when mixed solutions of sodic and potassic sulphate are allowed to crystallize. At the moment of crystallizing, the salt emits flashes of light, visible in the dark, the phenomenon being most striking when the temperature of the solution is about 40° C.

Sodic sulphite, $\mathbf{S}ONao_2,7\mathbf{O}H_2$, forms monoclinic crystals, readily soluble in water and possessing an alkaline reaction. When the solution is heated, it deposits an anhydrous salt, which dissolves again on cooling. *Hydric sodic sulphite*, $\mathbf{S}OHoNao$, crystallizes in small lustrous prisms, readily soluble in water, and possessing an acid reaction. The salt evolves sulphurous anhydride when exposed to the air, and is spontaneously oxidized to sulphate. *Sodic pyrosulphite*, $\mathbf{S}_2O_5Nao_2$, is

* In the aquates the symbol "aq." is frequently employed to denote a molecule of water of crystallization.

also known. The sulphites of sodium are prepared like the corresponding potassium salts (p. 418).

Sodic dithionate, $\left\{\begin{matrix}SO_2Nao\\SO_2Nao\end{matrix}\right.,2OH_2$, is prepared like the potassium salt (p. 419). It forms transparent rhombic prisms, readily soluble in water.

SODIC THIOSULPHATE (*Sodic hyposulphite*), $SO_2NaoNas,5OH_2$. (Preparation, see p. 277.) This salt is obtained on a large scale from *soda waste*, the insoluble matter which remains after the extraction of the sodic carbonate from the *black ash* in Leblanc's process. By exposing this residue in a moist condition to the air, the calcic sulphide (or oxysulphide) which it contains is oxidized to calcic thiosulphate, calcic hydrate being formed at the same time:

$$\underset{\text{Calcic sulphide.}}{2CaS''} + 2O_2 + \underset{\text{Water.}}{OH_2} = \underset{\text{Calcic thiosulphate.}}{SO_2\left(\begin{matrix}O\\S\end{matrix}Ca\right)} + \underset{\text{Calcic hydrate.}}{CaHo_2}.$$

The calcic thiosulphate is extracted with water and decomposed with sodic sulphate, thus yielding sodic thicsulphate and insoluble calcic sulphate. Sodic thiosulphate forms large, well defined monoclinic crystals, readily soluble in water and somewhat deliquescent. It fuses at 56° C. (133° F.) in its water of crystallization. When the dry salt is heated it is decomposed like the potassium salt (p. 419) into a mixture of sulphate and sulphide. The aqueous solution dissolves the chloride, bromide, and iodide of silver, a property which has caused the salt to be employed in fixing photographic prints. Sodic thiosulphate is also used as an *antichlore*, to destroy the excess of the chlorine employed in bleaching vegetable fibre.

Sodic selenate, $SeO_2Nao_2,10OH_2$, is prepared like the potassium salt (p. 419). It closely resembles sodic sulphate in its properties.

Sodic tellurate, TeO_2Nao_2, resembles the potassium salt.

SODIC PHOSPHATES:

a. Sodic phosphate, $PONao_3,12OH_2$, is prepared by fusing 2 molecules of hydric disodic phosphate with 1 molecule of sodic carbonate, dissolving in water and crystallizing; or by evaporating a solution of hydric disodic phosphate in caustic soda. The salt crystallizes in thin six-sided prisms, readily soluble in water, efflorescent in dry air. The solution, which has a strong alkaline reaction, absorbs carbonic anhydride from the air, the third atom of sodium being thus abstracted to form carbonate, whilst hydric disodic phosphate remains.—*Hydric disodic phosphate* ("*phosphate of soda*") $POHoNao_2,12OH_2$, is obtained by adding sodic carbonate or sodic hydrate to orthophosphoric acid until the liquid has a slight alkaline reaction, and then evaporating to the crystallizing point. On a large scale the orthophosphoric acid for this purpose is obtained by decomposing bone-ash with the requisite quantity of dilute sulphuric acid and filtering from the insoluble calcic sulphate. The salt forms efflorescent monoclinic prisms, soluble in 4.5–5

parts of water at ordinary temperatures. The solution has a weak alkaline reaction. At 37° C. (99° F.) the crystals fuse in their water of crystallization. At temperatures above 30° C. (86° F.) the solution deposits non-efflorescent crystals of a salt with 7 aq. When heated to redness hydric disodic phosphate parts with the elements of water, forming *tetrasodic pyrophosphate*, $\mathbf{P}_2O_3Nao_4$. Hydric sodic phosphate was formerly much used in calico-printing under the name of "dung substitute," but is now superseded by the cheaper sodic arsenate.—*Dihydric sodic phosphate*, $\mathbf{P}OHo_2Nao,\mathbf{O}H_2$, is obtained by adding phosphoric acid to the disodic salt until the solution no longer yields a precipitate with baric chloride, and then evaporating. It crystallizes in rhombic prisms, readily soluble in water, yielding an acid solution.

Hydric potassic sodic phosphate, $\mathbf{P}OHoKoNao,7\mathbf{O}H_2$, is prepared by adding potassic carbonate to a solution of dihydric sodic phosphate until the liquid has a slight alkaline reaction. It forms soluble monoclinic crystals.

b. Sodic pyrophosphate, $\mathbf{P}_2O_3Nao_4,10\mathbf{O}H_2$, is prepared by heating hydric disodic phosphate to redness, dissolving the mass in water and allowing to crystallize (p. 355). It is thus obtained in large monoclinic crystals, soluble in 10–12 parts of water at ordinary temperatures, and in their own weight of water at 100° C. The aqueous solution may be boiled without alteration, but when boiled with hydrochloric, nitric, or even acetic acid, the salt takes up the elements of water, at the same time parting with a portion of its base to the acid, and is converted into dihydric sodic phosphate.—*Dihydric disodic pyrophosphate*, $\mathbf{P}_2O_3Ho_2Nao_2$, separates as a crystalline powder when alcohol is added to a solution of the normal pyrophosphate in acetic acid. It may be boiled with water without decomposition.

Dipotassic disodic pyrophosphate, $\mathbf{P}_2O_3Ko_2Nao_2$, is obtained by neutralizing a solution of the acid sodium salt with potassic carbonate. It forms soluble acicular crystals.

c. Sodic metaphosphate, $\mathbf{P}O_2Nao$, is prepared by igniting either dihydric sodic phosphate, or hydric ammonic sodic phosphate, or dihydric disodic pyrophosphate (see *Metaphosphates*, p. 354). According to the temperature to which the substance has been heated and the rate of cooling, products differing widely in their properties, but all possessing the same percentage composition, are obtained. When the substance is heated to redness and rapidly cooled, the product is a vitreous deliquescent mass, which dissolves readily in water and remains behind on evaporation in the form of an uncrystallizable gum. If the cooling has been effected more slowly, there is formed, in addition to the uncrystallizable salt, a compound which is deposited from the solution in monoclinic prisms of the formula $\mathbf{P}O_2Nao,2\mathbf{O}H_2$. A third modification is obtained by limiting the temperature to 315° C. (599° F.). On extracting with water, an almost insoluble metaphosphate remains as a white powder. These differences are supposed to depend upon polymeric modification (see p. 354.)

Sodic arsenates.—The sodic arsenates are prepared like the phosphates, which they also resemble in properties. *Sodic arsenate*, $\mathbf{As}ONao_3,12\mathbf{O}H_2$, is very soluble in water, and is converted by the carbonic anhydride of the air into the monohydric salt. *Hydric disodic arsenate*, $\mathbf{As}OHoNao_2,12\mathbf{O}H_2$, closely resembles the corresponding phosphate, crystallizing in large efflorescent monoclinic prisms. Like the phosphate, it may be obtained from hot solutions in non-efflorescent crystals with 7 aq. At a red heat it parts with the elements of water, yielding *sodic pyrarsenate*, $\mathbf{As}_2O_3Nao_4$, which, however, cannot exist in solution, but, in contact with water, at once regenerates hydric disodic arsenate. *Dihydric sodic arsenate*, $\mathbf{As}OHo_2Nao,\mathbf{O}H_2$, obtained by adding arsenic acid to sodic carbonate till the solution no longer precipitates baric chloride, forms large soluble rhombic prisms.

Sodic antimonate.—When a solution of dihydric dipotassic pyrantimonate is added to the solution of a sodium salt, a granular crystalline precipitate of *dihydric disodic pyrantimonate*, $\mathbf{Sb}_2O_3Ho_2Nao_2\ 6\mathbf{O}H_2$, is produced. This salt is insoluble in water.

Sodic antimonite.—A solution of antimonious anhydride in caustic soda deposits lustrous rhombic octahedra of *sodic metantimonite*, $\mathbf{Sb}ONao,3\mathbf{O}H_2$, almost insoluble in cold, sparingly soluble in boiling water. Very concentrated solutions sometimes deposit rhombic prisms of *dihydric sodic trimetantimonite*, $\mathbf{Sb}_3O_3Ho_2Nao$.

SODIC BORATE.—The *metaborate*, $\mathbf{B}ONao,4\mathbf{O}H_2$, is prepared by fusing together equal molecules of boric anhydride and sodic carbonate, or by boiling a solution of borax with the necessary quantity of sodic hydrate, evaporating to a syrup and allowing to crystallize over sulphuric acid. It forms large triclinic crystals, readily soluble in water. The solution has an alkaline reaction, and absorbs carbonic anhydride from the air. A metaborate with 2 aq. is obtained in long acicular crystals by fusing the above salt in its water of crystallization and then allowing it to crystallize, or by crystallizing in presence of a large excess of sodic hydrate.—*Sodic tetraborate* (*borax*), $\mathbf{B}_4O_5Nao_2,10\mathbf{O}H_2$. This salt occurs in the water of some lakes in Thibet, from which it is obtained by evaporation and crystallization. The natural product, known as *tincal*, formed at one time the chief supply of this salt; but at present most of the borax of commerce is prepared from the boric acid obtained from the lagoons of Tuscany (p. 191.) The boric acid is either added to a boiling solution of sodic carbonate, or boric acid is heated with half its weight of anhydrous sodic carbonate, in a reverberatory furnace, and the mass, after cooling, extracted with water. The salt crystallizes in monoclinic prisms, soluble in 14 parts of water at ordinary temperatures and in half their weight of water at 100° C. The solution has an alkaline reaction. At temperatures above 60° C. (140° F.) borax crystallizes from concentrated solutions in regular octahedra, with 5 aq. (octahedral borax). When heated borax parts with its water of crystallization, intumescing and forming a porous white mass, which, at a higher temperature, fuses to a clear glass. In a state of fusion, it dissolves metallic oxides, with many of which it yields characteristically colored fluxes. This property, which depends upon the presence of an excess of boric anhydride in the salt, is utilized in the employment of borax as a blowpipe reagent. It is also used in soldering oxidizable metals, to dissolve the oxide in order to expose clean metallic surfaces. Further applications are: in various metallurgical operations as a flux, in the preparation of enamels, and in fixing colors on porcelain.

Sodic silicate, $\mathbf{Si}ONao_2,8\mathbf{O}H_2$, is prepared by dissolving 1 molecule of amorphous silicic anhydride in a solution of 2 molecules of sodic hydrate, evaporating to a syrup, and cooling by means of a freezing mixture, stirring at the same time. The salt, after

being purified by recrystallization, forms large monoclinic crystals, very soluble in water. Both in solution and in the dry state it absorbs carbonic anhydride from the air, undergoing decomposition, with separation of amorphous silicic acid. *Soluble soda glass* may be obtained in the same manner as the potassium compound. On a large scale it is prepared by heating together 100 parts of quartz sand, 60 parts of anhydrous sodic sulphate, and 15 to 20 parts of charcoal dust. The charcoal, by taking up part of the oxygen of the sulphate, facilitates the decomposition of this salt by the silicic anhydride. Soluble soda glass is employed as a cement, in coating building stone in order to preserve it from decay, and in fixing colors in fresco paintings. The alkaline silicates are important constituents of glass (*q.v*).

COMPOUNDS OF SODIUM WITH SULPHUR AND HYDROSULPHYL.

Sodic sulphide, Sodic polysulphides, and *Sodic sulphhydrate.*—These compounds are prepared like the corresponding potassium compounds, which they closely resemble.

SULPHO-SALTS OF SODIUM.

Sodic sulpharsenate, $2\mathbf{As}S''Nas_3,15\mathbf{O}H_2$, is prepared like the potassium compound. It forms large, colorless monoclinic prisms, readily soluble in water.

Sodic sulphantimonate (*Schlippe's salt*), $\mathbf{Sb}S''Nas_3,9\mathbf{O}H_2$, is obtained like the potash salt. It crystallizes in large pale yellow tetrahedra, readily soluble in boiling water. When exposed to the air, the crystals undergo superficial decomposition, becoming coated with a reddish-brown layer of antimonic sulphide.

COMPOUNDS OF SODIUM WITH NITROGEN AND HYDROGEN.

Sodic amide, $\mathbf{N}NaH_2$, is formed when sodium is gently warmed in a current of dry gaseous ammonia. The sodium fuses, yielding a greenish-blue liquid, which, on cooling, solidifies to a crystalline mass, whilst the color at the same time changes, through brown and olive-green, to a flesh tint. In presence of moisture and under the influence of heat, it behaves like potassic amide (pp. 423, 424).

General Properties and Reactions of the Compounds of Sodium.—The salts of sodium are as a rule more soluble than those of potassium. The only insoluble sodium salt is the dihydric disodic pyrantimonate ($\mathbf{Sb}_2O_3Ho_2Nao_2,6\mathbf{O}H_2$) (p. 434). Sodium compounds color the non-luminous flame an intense yellow. The color is invisible when a piece of cobalt glass or a solution of indigo is interposed between the flame and the eye. The flame spectrum of sodium consists of a double line in the yellow, coincident with D in the solar spectrum.

LITHIUM, Li_2?

Atomic weight = 7. *Probable molecular weight* = 14. *Sp. gr* = 0.59. *Fuses at* 180° C. (356° F.). *Atomicity* '. *Evidence of atomicity:*

Lithic chloride, ...	LiCl.
Lithic hydrate (lithia), ...	$\mathbf{O}$LiH.

History.—Lithic hydrate was discovered by Arfvedson in 1817. The metal was first isolated by Bunsen.

Occurrence.—Lithium is a constituent of several rare minerals, such as *lepidolite* (lithia mica), *petalite*, *spodumene*, and *triphyline*. By the aid of spectrum analysis, lithium has been shown to be very widely dis-

tributed: thus it occurs in minute quantities in the ashes of plants and in many mineral waters.

Preparation.—Metallic lithium cannot, like potassium or sodium, be reduced from its oxygen compounds by heating with charcoal. It is obtained by the electrolysis of the fused chloride. For this purpose a battery power of five or six Grove's cells is required. The positive pole is of hard gas coke, the evolved chlorine having no action upon this substance; for the negative pole, an iron wire is employed. A globule of molten metallic lithium soon forms on the iron wire under the surface of the fused chloride. As soon as this globule has attained the size of a pea, it is lifted out of the chloride along with the iron wire by means of a small iron spoon, a coating of lithic chloride protecting it from instantaneous oxidation, and is allowed to cool under petroleum. The globule is then detached from the wire and these operations are repeated until a sufficient quantity of the metal has been obtained. The globule must not be permitted to attain too great a size, otherwise it will detach itself from the iron wire and rise to the surface of the fused chloride, where it generally inflames.

Properties.—Lithium is a silver-white metal, harder than potassium or sodium, but softer than lead. It has a sp. gr. of 0.59, and is thus the lightest solid known. It floats on petroleum. It is less oxidizable than potassium or sodium, but speedily tarnishes when exposed to the air. Heated in air to a temperature considerably above its fusing-point, it inflames, burning with an intense white light. It decomposes water, without however inflaming, even when the water is hot. The solution contains lithic hydrate, LiHo.

COMPOUNDS OF LITHIUM WITH THE HALOGENS.

These compounds are prepared by dissolving the hydrate or carbonate in the corresponding hydracid.

LITHIC CHLORIDE, LiCl, crystallizes in anhydrous octahedra, having the taste of common salt. At temperatures below 10° C. (50° F.) it crystallizes with 2 aq. It is deliquescent and readily soluble in alcohol or in a mixture of alcohol and ether, by which means it may be separated from the other chlorides of this group. It volatilizes below a red heat.

Lithic iodide, $LiI,3OH_2$, forms very deliquescent needles.

Lithic fluoride, LiF, crystallizes in small opaque white granular crystals, sparingly soluble in water.

COMPOUNDS OF LITHIUM WITH OXYGEN AND HYDROXYL.

Lithic oxide, OLi_2, is obtained as a white spongy mass, containing a certain quantity of a higher oxide, by burning lithium in dry oxygen.

Lithic hydrate (*Lithia*), LiHo, is prepared like the hydrate of potassium, which it also resembles in most of its properties. It is, however,

less soluble in water than potassic hydrate, and does not deliquesce when exposed to the air. Fused lithic hydrate corrodes platinum powerfully, and should therefore always be prepared in a silver capsule.

OXY-SALTS OF LITHIUM.

These are for the most part obtained by neutralizing the acid with lithic hydrate or carbonate.

Lithic nitrate, NO_2Lio, crystallizes at 15° C. (59° F.) in anhydrous rhombohedra, below 10° C. (50° F.) in thin prisms of the formula $2NO_2Lio,5OH_2$. It is deliquescent and very soluble in water.

Lithic perchlorate, $\begin{cases} OCl \\ O \\ OLio \end{cases}$, is a deliquescent salt, readily soluble in alcohol.

Lithic carbonate, $COLio_2$, occurs in small quantities in various mineral waters. It is prepared by precipitating a solution of lithic chloride or nitrate with potassic, sodic, or ammonic carbonate. It is thus obtained as a white crystalline powder, sparingly soluble in cold water. The solution is alkaline and deposits the salt by slow evaporation in small prisms. At a bright red heat lithic carbonate undergoes partial decomposition, evolving carbonic anhydride. Owing to its insolubility, this salt is frequently employed in separating lithium from potassium and sodium.

Lithic sulphate, SO_2Lio_2,OH_2, forms flat, monoclinic prisms or tables, readily soluble in water, soluble also in alcohol.

Potassic lithic sulphate, $S_3O_6Ko_4Lio_2$.—Hexagonal crystals.

Lithic dithionate, $\begin{cases} SO_2Lio \\ SO_2Lio \end{cases},2OH_2$, is prepared by exactly precipitating a solution of baric dithionate with lithic sulphate and evaporating the resulting solution of lithic dithionate to crystallization. It forms large rhombic crystals, readily soluble in water and somewhat deliquescent. It is insoluble in alcohol.

Lithic phosphate, $2POLio_3,OH_2$, is precipitated, slowly in the cold, instantaneously on heating, when hydric disodic phosphate is added to a solution of a lithium salt. If the solution is rendered alkaline by the addition of sodic hydrate or carbonate, the precipitation of the lithium is complete. Lithic phosphate forms a white crystalline powder, very sparingly soluble in water (1 part of the salt requires 2500 parts of water at ordinary temperatures for solution), still less soluble in water containing ammonia. When heated, it parts with its water of crystallization, but does not fuse, even at a red heat. This salt is employed in the estimation of lithium.—*Dihydric lithic phosphate*, $POHo_2Lio$, is formed when either the preceding salt, or lithic carbonate, is dissolved in an excess of phosphoric acid and the solution evaporated. It is thus obtained in large, very soluble, deliquescent crystals, with an acid reaction.

General Properties and Reactions of the Compounds of Lithium.—Lithium is distinguished from the other metals of the alkali group by the sparing solubility of its normal carbonate and phosphate

and by the solubility of lithic chloride in a mixture of alcohol and ether. Lithium compounds color the non-luminous flame carmine-red. The spectrum of lithium displays a bright line Liα in the red, and a faint line Liβ in the yellow. At the temperature of the oxyhydrogen flame a brilliant blue line makes its appearance.

RUBIDIUM, Rb_2?

Atomic weight = 85.3. *Probable molecular weight* = 170.6. *Sp. gr.* 1.52. *Fuses at* 38.5° C. (101.3° F.). *Atomicity* $'$. *Evidence of atomicity:*

Rubidic chloride, ...	RbCl.
Rubidic iodide, ...	RbI.
Rubidic hydrate, ...	RbHo.

History.—Rubidium was discovered in 1860 by Bunsen and Kirchhoff with the aid of spectrum analysis.

Occurrence.—This rare metal is widely distributed in nature, but always in very minute quantity. It occurs along with potassium in many minerals (frequently in *lepidolite*), in the ashes of plants, and in some mineral springs. It was first obtained from the water of a spring at Dürkheim in Baden.

Preparation.—1. Metallic rubidium may be obtained by the electrolysis of the fused chloride as in the preparation of lithium (p. 436).

2. A more advantageous process consists in distilling a mixture of rubidic carbonate and carbon obtained by charring rubidic tartrate, as in the corresponding method for the preparation of potassium (p. 412).

Properties.—Rubidium is a lustrous white metal, with a yellowish tinge. It is soft like wax, even at —10° C. (14° F.). It fuses at 38.5° C. (101.3° F.), and boils below a red heat, yielding a greenish-blue vapor. Exposed to the air, it instantly becomes covered with a bluish-gray film of oxide and speedily inflames spontaneously. It burns, with vivid incandescence, in chlorine and in the vapors of bromine, iodine, sulphur, and arsenic. In contact with water it behaves like potassium.

COMPOUNDS OF RUBIDIUM.

RUBIDIC CHLORIDE, RbCl, crystallizes in transparent colorless cubes, possessing a vitreous lustre. It is more soluble than potassic chloride (100 parts of water at 7° C. dissolve 83 parts), and is easily fusible and volatile. It forms double salts with other metallic chlorides. The most important of these double chlorides is *rubidic platinic chloride* ($\mathbf{Pt}Cl_4$,2RbCl), which is even less soluble than the corresponding potassium compound, and is employed in the separation of rubidium.

Rubidic bromide, RbBr, crystallizes in lustrous cubes with subordinate octahedral faces, and is soluble in its own weight of water at ordinary temperatures.

Rubidic iodide, RbI, resembles the bromide. It dissolves in 0.7 part of water at ordinary temperatures.

Rubidic hydrate, RbHo, resembles the potassium compound, but is a more powerful base.

Rubidic nitrate, NO_2Rbo, forms hexagonal crystals, soluble in 2.3 parts of water at 10° C. (50° F.).

Rubidic chlorate, $\left\{\begin{matrix} OCl \\ ORbo \end{matrix}\right.$.—This salt forms small prismatic crystals, soluble in 20–25 parts of water at ordinary temperatures.

Rubidic perchlorate, $\left\{\begin{matrix} OCl \\ O \\ ORbo \end{matrix}\right.$, forms small hard lustrous rhombic crystals. It is less soluble than the corresponding potassium salt, 1 part of the salt requiring 92 parts of water at 21° C. (70° F.) for its solution.

Rubidic carbonate.—The *normal salt*, $CORbo_2.OH_2$, forms indistinct crystals with a strong alkaline reaction. The water of crystallization is expelled by heating. It is readily soluble in water. Exposed to the air it deliquesces and absorbs carbonic anhydride, forming the *acid salt* COHoRbo, which crystallizes in non-deliquescent prisms with a vitreous lustre.

Rubidic sulphate.—The *normal salt*, SO_2Rbo_2, crystallizes in large, hard, rhombic crystals with a vitreous lustre, more soluble in water than the potassium salt. The *acid salt*, SO_2HoRbo, forms short rhombic prisms.

Rubidic dithionate, $\left\{\begin{matrix} SO_2Rbo \\ SO_2Rbo \end{matrix}\right.$, forms hard, hexagonal crystals, with a vitreous lustre.

Rubidic borate.—A *tetraborate* of the formula $B_4O_5Rbo_2,6OH_2$ is known. It forms small lustrous crystals belonging to the rhombic system.

CÆSIUM, Cs_2?

Atomic weight = 133. *Probable molecular weight* = 266. *Sp. gr.* 1.88. *Fuses at* 26.5° C. (79.7° F.). *Atomicity* ′. *Evidence of atomicity:*

Cæsic chloride, ...	CsCl.
Cæsic hydrate, ...	CsHo.

History.—This metal, which is even rarer than rubidium, was discovered simultaneously with the latter in the water of the Dürkheim spring by Bunsen and Kirchhoff, in 1860.

Occurrence.—The rare mineral *pollux*, which occurs in the granite of Elba, is a silicate of aluminium, sodium, and cæsium, and contains 32 per cent. of the latter metal. In minute traces cæsium is found in a variety of minerals, and in many mineral springs.

Preparation.—Metallic cæsium cannot be obtained by the methods usually employed in the isolation of the alkali metals. Heating the oxide or carbonate with charcoal yields no result; whilst, in the electrolysis of the fused chloride, the reduced metal immediately acts upon the undecomposed chloride, yielding a blue compound of unknown composition—possibly a subchloride. If, however, fused cæsic cyanide, Cs(CN), mixed with a quarter of its weight of baric cyanide, $Ba(CN)_2$, in order to increase the fusibility, be subjected to electrolysis, pure metallic cæsium is obtained in coherent masses.

Properties.—Cæsium is a lustrous white metal. At ordinary tem-

peratures it is soft. It fuses at 26.5° C. (79.7° F.). When exposed to the air it oxidizes rapidly, and finally inflames spontaneously. Thrown on to water it behaves like potassium. Cæsium is the most electro-positive of the elements.

COMPOUNDS OF CÆSIUM.

CÆSIC CHLORIDE, CsCl, crystallizes in indistinct cubes, which are very soluble and deliquescent. It fuses below redness, and is more easily volatilized than potassic chloride. When heated in moist air it is partially converted into hydrate. It forms double salts with other metallic chlorides. *Cæsic antimonious chloride* ($\mathbf{Sb}Cl_3$,CsCl) is obtained as a white crystalline precipitate by the addition of antimonious chloride dissolved in hydrochloric acid to a solution of cæsic chloride. *Cæsic platinic chloride* ($\mathbf{Pt}Cl_4$,2CsCl) forms a yellow crystalline precipitate, even less soluble than the corresponding rubidium salt.

Cæsic hydrate, CsHo, is a caustic, crystalline substance resembling potassic hydrate.

Cæsic nitrate, $\mathbf{N}O_2$Cso, crystallizes in hexagonal prisms, and is less soluble in water than the potassium salt.

Cæsic carbonate.—Both the normal and the acid carbonate resemble in almost every respect the rubidium salts. The normal carbonate is soluble in alcohol.

Cæsic sulphate.—The *normal salt*, $\mathbf{S}O_2Cso_2$, forms prismatic crystals very soluble in water. *Hydric cæsic sulphate*, $\mathbf{S}O_2$HoCso, crystallizes in small rhombic prisms.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF RUBIDIUM AND CÆSIUM.—The salts of rubidium and cæsium cannot be distinguished from those of potassium by the ordinary chemical tests. Like these they yield precipitates with *platinic chloride* and *tartaric acid*. Cæsic platinic chloride ($\mathbf{Pt}Cl_4$,2CsCl) is more difficultly soluble in boiling water than rubidic platinic chloride ($\mathbf{Pt}Cl_4$2RbCl), and this again is more difficultly soluble than the potassium compound. In this way a separation of the three metals may be effected. Cæsium may also be separated from rubidium by the solubility of its normal carbonate in alcohol. The flame colorations of the cæsium and rubidium compounds resemble closely that of potassium. By means of the characteristic spectra, however, the compounds of the three metals may be readily distinguished. The spectrum of rubidium consists of two lines, Rbα and Rbβ, in the violet, and two lines, Rbδ and Rbγ, in the red, together with other fainter lines. The most characteristic lines in the spectrum of cæsium are Csα and Csβ in the blue.

THE AMMONIUM SALTS.

The hypothetical radical ammonium $\left\{ \begin{matrix} \mathbf{N}H_4 \\ \mathbf{N}H_4 \end{matrix} \right.$ has already been referred to (p. 235) in connection with the compounds of nitrogen. Its salts closely resemble those of the alkalies, and may therefore be appropriately treated of at this point.

COMPOUNDS OF AMMONIUM WITH THE HALOGENS.

AMMONIC CHLORIDE, NH_4Cl.—This compound occurs in small quantities in the neighborhood of volcanoes, being generally formed when lava flows over fertile land. The nitrogenous vegetable mater, thus subjected to a destructive distillation, furnishes ammonia, the latter combining with the hydrochloric acid which is almost always present in volcanic gases. Ammonic chloride is prepared by neutralizing the ammoniacal liquor from the gas-works—the ammonia being in this case a product of the destructive distillation of fossil vegetable matter—with hydrochloric acid, and purifying the crude ammonic chloride by crystallization and sublimation. The aqueous portion of the distillate obtained in the preparation of animal charcoal from bones is also very rich in ammonia, and serves as a source of the chloride. Ammonic chloride crystallizes from water in small indistinct octahedra or cubes, which are generally grouped in fern-shaped aggregations. When heated, it does not fuse, but sublimes, undergoing dissociation into ammonia and hydrochloric acid, which again unite as the temperature falls. When sublimed in large quantities, it forms semi-transparent, tough, fibrous masses. Dissociation also takes place when a neutral solution of the salt is boiled: a small quantity of ammonia passes off with the steam, and free hydrochloric acid is found in the solution. In presence of an excess of hydrochloric acid this dissociation does not occur, and solutions of ammonic chloride may be evaporated at 100° C. without loss. Ammonic chloride is soluble in $2\frac{1}{2}$ parts of water at ordinary temperatures and in its own weight of water at 100° C. Absolute alcohol does not dissolve it. Ammonic chloride forms double salts with various metallic chlorides: *ammonic platinic chloride*, $PtCl_4,2NH_4Cl$, crystallizes in minute octahedra, almost insoluble in water, and insoluble in a mixture of alcohol and ether. This double salt, which closely resembles the corresponding potassium compound, is employed in the quantitative determination of ammonia. When heated, the double salt is decomposed, platinum being left behind in the finely divided condition in which it is known as spongy platinum. Ammonic chloride has numerous uses. It is employed in medicine, in dyeing, in soldering, and tinning—in which last process it serves to produce a clean metallic surface, either by reducing the oxides at a high temperature, or by converting them into fusible chlorides—in the preparation of ammonia and ammonic carbonate, as a laboratory reagent, and as a manure.

Ammonic bromide, NH_4Br.—This compound is prepared by the direct union of hydrobromic acid with ammonia, or by the addition of bromine to aqueous ammonia, nitrogen being evolved in the latter reaction:

$$\underset{\text{Ammonia.}}{4NH_3} + 3Br = \underset{\text{Ammonic bromide.}}{3NH_4Br} + N.$$

It crystallizes in colorless cubes, readily soluble in water, less soluble in alcohol. The crystals become moist in contact with the air, and

assume a yellow color, owing to the separation of bromine. It sublimes without fusing.

Ammonic iodide, $\mathbf{N}H_4I$.—This salt is prepared by the direct union of ammonia and hydriodic acid, or more conveniently by adding to a hot saturated solution of potassic iodide the equivalent quantity of ammonic sulphate, precipitating the potassic sulphate with alcohol, and evaporating the solution. It crystallizes in colorless cubes, readily soluble in water and in alcohol. It may be sublimed in an atmosphere free from oxygen. Exposed to the air, it assumes a yellow color, due to the liberation of iodine. Ammonic iodide is employed in photography.

Ammonic fluoride, $\mathbf{N}H_4F$, is obtained by evaporating a solution of hydrofluoric acid supersaturated with ammonia and kept alkaline with ammonia during the evaporation, or by heating in a platinum vessel a mixture of 1 part of ammonic chloride with $2\frac{1}{4}$ parts of sodic fluoride, when the ammonic fluoride sublimes and condenses in crystals on the cooled lid of the vessel. It crystallizes in colorless hexagonal prisms or laminæ, deliquescent in moist air, readily soluble in water, sparingly soluble in alcohol. On evaporation, the neutral aqueous solution gives off ammonia and yields rhombic prisms of *hydric ammonic fluoride*, $\mathbf{N}H_4F,HF$. Dry ammonic fluoride absorbs gaseous ammonia, which it again parts with on heating. The dry salt decomposes silicates when heated with them. Ammonic fluoride is employed in etching glass. *Ammonic silicofluoride*, $SiF_6(NH_4)_2$, is readily soluble in water.

COMPOUND WITH HYDROXYL.

Ammonic hydrate, $\mathbf{N}H_4Ho$.—This compound has not been isolated, but may be considered to exist in the aqueous solution of ammonia, which is powerfully alkaline, slightly caustic, and possesses the other properties of the solutions of the alkaline hydrates.* On evaporation the ammonic hydrate undergoes dissociation into ammonia and water: $\mathbf{N}H_4Ho = \mathbf{N}H_3 + \mathbf{O}H_2$. (For the other properties of aqueous ammonia, see p. 232.)

Ammonic oxide, $\mathbf{O}(N^{v}H_4)_2$, is unknown.

OXY-SALTS OF AMMONIUM.

These are, as a rule, prepared by neutralizing aqueous ammonia or ammonic carbonate with the oxy-acid. Special methods will be described under the corresponding salts.

Ammonic nitrate, $\mathbf{N}O_2(N^{v}H_4O)$, or $\mathbf{N}O_2Amo$, forms six-sided prisms belonging to the rhombic system. It dissolves in about half its weight of water at 18° C. (64° F.), with great absorption of heat.

* Kohlrausch, however, finds that, whereas the ammonic salts, when in solution, possess the same electrolytic conductivity as the corresponding potassium salts, aqueous ammonia is a bad conductor of the current, whilst a solution of potassic hydrate conducts the current well. From this he concludes that an aqueous solution of ammonia contains little or no ammonic hydrate.

In moist air it deliquesces, at the same time losing ammonia and becoming acid. When heated, it is decomposed into nitrous oxide and water (p. 220). At low temperatures it absorbs gaseous ammonia with great avidity, taking up at — 10° C. (14° F.) two molecules of ammonia, and yielding a compound of the formula $\mathbf{N}(NH_2)_2Ho_2Amo$. This substance is a colorless liquid of sp. gr. 1.05, which does not solidify at — 18° C. (0° F.). As the temperature rises this compound dissociates, till at 28.5° C. (83.3° F.) it parts with one molecule of ammonia, and is converted into a white crystalline mass, of the formula $\mathbf{N}O(NH_2)HoAmo$. This substance also suffers dissociation as the temperature rises, giving off ammonia and yielding at 80° C. (176° F.) pure ammonic nitrate.

AMMONIC NITRITE, $\mathbf{N}OAmo$, is formed in small quantity when phosphorus undergoes slow oxidation in contact with moist air; also during the combustion of hydrogen or hydrogenous substances in air, and by the action of ozone on dilute ammonia. It may be obtained in crystals by passing simultaneously ammonia, nitric oxide, and oxygen into a dry flask. It is most easily prepared by the double decomposition of argentic nitrite with ammonic chloride, or of baric nitrite with ammonic sulphate, the solution obtained by either of these methods being filtered from the insoluble precipitate and evaporated in a desiccator over quickline. Thus obtained it forms a crystalline, very soluble mass. It decomposes slowly at ordinary temperatures into nitrogen and water (p. 212). When heated to 60–70° C. (140–158° F.), or when struck, it detonates. In concentrated aqueous solution it undergoes rapid decomposition, the process being accelerated by heat and retarded by dilution.

Ammonic chlorate, $\left\{\begin{array}{l}\mathbf{O}Cl\\ \mathbf{O}Amo\end{array}\right.$, is prepared by neutralizing chloric acid with ammonia or ammonic carbonate, or by the double decomposition of ammonic silicofluoride with potassic chlorate, filtering from the insoluble potassic silicofluoride and evaporating over sulphuric acid. It crystallizes in colorless prisms or slender needles, readily soluble in water or alcohol. When dry the crystals turn yellow and frequently explode spontaneously with great violence. This explosive decomposition takes place at once on heating to somewhat above 100° C. The aqueous solution on boiling evolves nitrogen and chlorine.

Ammonic perchlorate, $\left\{\begin{array}{l}\mathbf{O}Cl\\ O\\ \mathbf{O}Amo\end{array}\right.$.—Large rhombic crystals, soluble in 5 parts of water.

Ammonic bromate, $\left\{\begin{array}{l}\mathbf{O}Br\\ \mathbf{O}Amo\end{array}\right.$, forms white needles or crystalline granules. The dry salt explodes spontaneously like the chlorate.

Ammonic iodate, $\left\{\begin{array}{l}\mathbf{O}I\\ \mathbf{O}Amo\end{array}\right.$.—Lustrous quadratic crystals, soluble in 38 parts of water at ordinary temperatures and in 6.9 parts of boiling water. At 150° C. (302° F.) it decomposes with a hissing noise, yielding equal volumes of oxygen and nitrogen, together with iodine and water.

AMMONIC CARBONATE:

Normal ammonic carbonate, $\mathbf{C}OAmo_2$.—This salt is deposited as a crystalline powder when a concentrated solution of the sesquicarbonate (*vide infra*) is saturated with gaseous ammonia, and in large tabular crystals when a hot solution of the sesquicarbonate in dilute aqueous

ammonia is allowed to cool. It is a very unstable salt. When exposed to the air it rapidly parts with ammonia and is converted into *hydric ammonic carbonate*, COHoAmo. It dissociates completely at 58° C. (136° F.) into carbonic anhydride, ammonia, and water. It is soluble at ordinary temperatures in its own weight of water, but only sparingly soluble in concentrated ammonia.—*Hydric ammonic carbonate*, COHoAmo, occurs in a crystallized form in guano beds. It may be obtained from the commercial sesquicarbonate either by exposing the latter salt to the air, when it parts with ammonia, yielding the acid carbonate; or by treating the sesquicarbonate with a small quantity of water, which dissolves the normal carbonate, leaving the acid carbonate. It is also deposited when a concentrated solution of the sesquicarbonate is exposed to a low temperature, or is mixed with alcohol, or is saturated with carbonic anhydride. It crystallizes in hard lustrous rhombic prisms. It sublimes at 60–65° C. (140–149° F.). It dissolves in about 8 parts of water at ordinary temperatures. The solution slowly evolves carbonic anhydride and becomes ammoniacal. This decomposition is very rapid above 36° C. (97° F.), the liquid effervescing when warmed. It is insoluble in alcohol, but on long standing under alcohol dissolves as normal carbonate, with evolution of carbonic anhydride.

Ammonic sesquicarbonate, $COAmo_2$,2COHoAmo.—This salt is prepared on a large scale by heating ammonic chloride or sulphate with calcic carbonate, when the sesquicarbonate sublimes. It forms a translucent, crystalline mass, which is usually coated with an opaque layer of the acid carbonate. Its composition varies, generally approximating however to the above formula. It has an ammoniacal odor, and is gradually converted by exposure to air into the acid salt.

AMMONIC SULPHATE:

Ammonic sulphate, SO_2Amo_2, is found native as *mascagnine*. It is prepared on a large scale by passing the ammonia from the ammoniacal liquors of the gasworks into sulphuric acid. It forms colorless rhombic crystals, isomorphous with the potassium salt. It is soluble in twice its weight of cold, in its own weight of boiling, water; insoluble in alcohol. It fuses at 140° C. (284° F.), and above 280° C. (536° F.) is decomposed into ammonia, nitrogen, water, and ammonic sulphite, the latter subliming.—*Hydric ammonic sulphate*, SO_2HoAmo, crystallizes from a solution of the normal salt in concentrated sulphuric acid in deliquescent thin rhombic crystals. It is soluble in its own weight of cold water, also in alcohol.

Ammonic sulphate is employed in the manufacture of ammonia-alum; also as a manure.

Ammonic potassic sulphate, SO_2AmoKo, is obtained by evaporating a solution of molecular quantities of ammonic potassic sulphates. It crystallizes in lustrous scales.

Ammonic sodic sulphate, SO_2AmoNao,$2OH_2$, is prepared like the foregoing. It is also deposited in crystals when mixed solutions of sodic sulphate and ammonic chloride, or of sodic chloride and ammonic sulphate, are evaporated. The salt is permanent in air.

Ammonic sulphite, $SOAmo_2,OH_2$, is obtained by neutralizing an aqueous solution of sulphurous anhydride with ammonia, and then adding alcohol. The salt separates in monoclinic crystals, readily soluble in water. By exposure to the air it is oxidized to

ammonic sulphate. When a solution of this salt is saturated with sulphurous anhydride and evaporated over sulphuric acid, it deposits crystals, not of the acid salt, but of *ammonic pyrosulphite*, $\left\{\begin{array}{l}SOAmo\\O\\SOAmo\end{array}\right.$. This salt evolves sulphurous anhydride when exposed to the air, at the same time undergoing oxidation to ammonic sulphate.

Ammonic dithionate, $\left\{\begin{array}{l}SO_2Amo\\SO_2Amo\end{array}\right.,OH_2$, is obtained by the double decomposition of baric dithionate with ammonic sulphate. It forms colorless capillary crystals, very soluble in water, insoluble in alcohol.

Ammonic thiosulphate (*Ammonic hyposulphite*), $3SO_2AmoAms,OH_2$, is prepared by decomposing calcic thiosulphate with ammonic carbonate. It forms deliquescent, very soluble acicular crystals or rhombic plates.

AMMONIC PHOSPHATE:

a. Ammonic phosphate, $POAmo_3,3OH_2$, occurs sometimes in guano. It is formed when a concentrated solution of hydric diammonic phosphate is mixed with ammonia, and is deposited in small prismatic or acicular crystals, which when exposed to the air part with ammonia, yielding hydric diammonic phosphate. When boiled for some time in aqueous solution, it is converted into dihydric ammonic phosphate. When strongly heated, it yields, like all the other ammonic phosphates, metaphosphoric acid.—*Hydric diammonic phosphate*, $POHoAmo_2$, is prepared by evaporating an ammoniacal solution of phosphoric acid, care being taken to keep the ammonia slightly in excess during the process. It forms large colorless monoclinic crystals, soluble in 4 parts of cold, more readily in boiling, water; insoluble in alcohol. Exposed to the air it gradually parts with ammonia.—*Dihydric ammonic phosphate*, $POHo_2Amo$, is prepared by adding phosphoric acid to ammonia till the solution is strongly acid and no longer precipitates baric chloride, and evaporating to the crystallizing point; or by boiling a solution of the monohydric salt. It crystallizes in quadratic octahedra, which are permanent in air. It is somewhat less soluble than the foregoing salt.

Hydric ammonic sodic phosphate (*Microcosmic salt*),

$$POHoAmoNao,4OH_2.—$$

This salt occurs in guano and in putrid urine. It is prepared by dissolving 6 parts of hydric disodic phosphate and 1 part of ammonic chloride in 2 parts of boiling water, and allowing the liquid to cool. It forms large colorless monoclinic prisms, very soluble in water, yielding a solution which gives off a portion of its ammonia on evaporation. It fuses easily, water and ammonia being expelled, and sodic metaphosphate left. Microcosmic salt is employed in the laboratory as a blowpipe reagent, the sodic metaphosphate, which remains on heating it, possessing the property of dissolving various metallic oxides at a high temperature to yield characteristically colored fluxes or glasses.

Diammonic sodic phosphate, $POAmo_2Nao,4OH_2$, separates in lustrous white pearly laminæ when strong ammonia is added to a cold saturated solution of the foregoing. It evolves ammonia when exposed to the air, and is converted into hydric ammonic sodic phosphate.

b. Ammonic pyrophosphate, $P_2O_3Amo_4$, separates in small acicular laminæ when alcohol is added to a solution of pyrophosphoric acid

supersaturated with ammonia. Its solution gives off ammonia when boiled, yielding *dihydric diammonic pyrophosphate*, $P_2O_3Ho_2Amo_2$, which may be precipitated from its solution by the addition of alcohol as a syrupy mass, becoming crystalline on standing.

c. *Ammonic metaphosphates* are also known.

Ammonic borate.—The normal salt has not been prepared. *Diammonic tetraborate*, $B_4O_5Amo_2,4OH_2$, crystallizes from a solution of boric acid in warm concentrated ammonia in quadratic crystals, which give off ammonia when exposed to the air. When this salt is dissolved in water and the solution evaporated by heat, colorless transparent rhombic crystals of *hydric ammonic tetraborate*, $B_4O_5HoAmo,3OH_2$, are deposited on cooling.

COMPOUNDS OF AMMONIUM WITH SULPHUR AND HYDROSULPHYL.

Ammonic sulphide, SAm_2, is obtained in lustrous crystals by the union of 2 volumes of ammonia with 1 volume of sulphuretted hydrogen at a temperature of —18° C. (0° F.). Above this temperature it dissociates, evolving amnonia, and yielding *ammonic sulphhydrate*, AmHs.

Ammonic sulphhydrate, AmHs, is formed by the direct union of equal volumes of ammonia and sulphuretted hydrogen at ordinary temperatures. It is best prepared by passing sulphuretted hydrogen into alcoholic ammonia, when the sulphhydrate separates out in a crystalline form. The aqueous solution employed as a laboratory reagent is obtained by saturating aqueous ammonia with sulphuretted hydrogen. Ammonic sulphhydrate forms large colorless laminæ. It volatilizes readily, with dissociation into ammonia and sulphuretted hydrogen, which reunite on cooling. It becomes yellow, both in the solid state and in solution, when exposed to the air, owing to the formation of polysulphides of ammonium. The solution precipitates many metals in the form of sulphides from the solution of their salts, and dissolves sulphur to form ammonic polysulphides.

Ammonic pentasulphide, Am_2S_5, is prepared by alternately passing ammonia and sulphuretted hydrogen into a mixture of ammonic sulphhydrate and flowers of sulphur until the liquid solidifies on cooling. The mixture is then heated to 50° C. (122° F.) and allowed to cool with exclusion of air, when the pentasulphide is deposited in orange-yellow rhombic prisms. Water decomposes them with precipitation of plastic sulphur.

Ammonic heptasulphide, Am_2S_7, is formed by the spontaneous decomposition of the foregoing compound in presence of air:

$$\underset{\text{Ammonic pentasulphide.}}{3(NH_4)_2S_5} = \underset{\text{Ammonic heptasulphide.}}{2(NH_4)_2S_7} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Ammonic sulphhydrate.}}{NH_4Hs.}$$

It forms ruby-red crystals, which are not decomposed by heat below 300° C. (572° F.), but are slowly decomposed by water.

General Properties and Reactions of the Ammonium Salts.—The ammonium salts are all volatile—some with decomposition, others with dissociation, in which last case the dissociated

constituents recombine on cooling to form the original salt, as in the case of ammonic chloride (p. 64). Ammonium salts yield with *platinic chloride* and with *tartaric acid* precipitates closely resembling those obtained with potassium salts; ammonic platinic chloride ($\mathbf{Pt}Cl_4,2\mathbf{N}H_4Cl$), however, leaves only a residue of spongy platinum on ignition. All ammonium salts, when warmed with *calcic hydrate*, or with concentrated *caustic potash* or *caustic soda*, evolve gaseous ammonia, which may generally be recognized by its characteristic smell, or in case the quantity is very minute, by the white fumes of ammonic chloride which are formed when a glass rod moistened with hydrochloric acid is held over the mixture. The smallest trace of ammonia in aqueous solution may be detected by means of a solution of mercuric iodide in a mixture of potassic iodide and caustic potash (Nessler's reagent), with which it yields a brown coloration, or, if present in larger quantity, a brown precipitate, of $\mathbf{N}Hg''(Hg''Ho)HI$. This reaction does not occur in presence of alkaline sulphides or cyanides.

MONAD METALS.

Section IV.

SILVER, Ag_2?

Atomic weight = 107.7. *Probable molecular weight* = 215.4. *Sp. gr.* 10.57. *Fuses at* 1040° C. (1904° F.). *Atomicity* '. *Evidence of atomicity:*

Argentic chloride, ...	$AgCl$.
Argentic iodide, ...	AgI.
Argentic oxide, ...	$\mathbf{O}Ag_2$.

History.—This metal has been known from the earliest times.

Occurrence.—Silver occurs native, occasionally in large masses. Native silver is rarely pure: it contains gold, copper, and other metals. In combination, silver occurs as argentic sulphide in *silver glance* ($\mathbf{S}Ag_2$); as sulphantimonite in *pyrargarite* or *dark-red silver ore* ($\mathbf{Sb}Ags_3$); as chloride in *kerargyrite* or *horn-silver* ($AgCl$). The bromide, iodide, telluride, antimonide, and arsenide are rare minerals. Galena, or plumbic sulphide, the commonest form of lead ore, generally contains small quantities of silver. Silver also occurs in minute traces in sea-water.

Extraction.—Although silver is very readily reducible from its compounds (the mere application of heat being generally sufficient for this purpose), yet the extraction of silver from its ores is a matter of considerable practical difficulty. The ores of silver are frequently mixed with earthy impurities, from which they cannot be mechanically separated, or they occur along with the ores of other metals, which are apt to undergo reduction at the same time, and thus contaminate the product. The process of extraction varies with the nature of the ore; but the methods employed may be divided into three classes according

as they depend upon *cupellation*, upon *amalgamation*, or upon reactions in the *wet way*.

a. Cupellation Process.—This process is employed in separating silver from lead. The alloy of silver and lead, obtained from argentiferous lead ores, is fused in a reverberatory furnace, the hearth of which is composed of burnt clay. Over the molten metal, which rests upon the concave surface of this hearth or cupel, a rapid current of air is blown. The lead is thus oxidized, and the fused oxide escapes by flowing off through lateral openings in the hearth, whilst the silver remains in the cupel. At first the fused oxide flows off in large quantity, but towards the end of the operation it forms thin films upon the surface of the silver, exhibiting the colors of Newton's rings. At last, as the film of oxide finally disappears, the bright surface of the silver is perceived. This phenomenon is known as the "fulguration" of the metal. The removal of the oxide is aided by skimming.

When the lead is sufficiently rich in silver, it is cupelled at once; but if the silver is present in a proportion less than one-tenth of a per cent., the lead is subjected to a preliminary process, which has for its object the concentration of the silver in a relatively small portion of the lead. In this process, invented by Pattinson, the metal is fused in iron pots and allowed to cool slowly. As soon as the temperature has sufficiently fallen, crystals of pure lead are formed; these are constantly removed by means of perforated ladles, and this is continued until the lead in the pot has been reduced in quantity by about two-thirds. In this way the greater part of the silver is left behind in the pot, and by systematic recrystallization, pure and nearly desilverized lead on the one hand, and a lead very rich in silver on the other, may be obtained. The rich lead is cupelled as above described.

Instead of treating the lead by Pattinson's process, it may be fused, and zinc, in the proportion of 11.2 lbs. for every 7 ozs. of silver present per ton of lead, added. The whole is thoroughly stirred and then allowed to settle. The zinc extracts the greater part of the silver from the lead and rises to the surface, where it solidifies first, and may be removed as a solid cake. This cake is then heated to redness in a current of air, by which means the zinc is converted into zincic oxide, and may be separated from the unaltered silver by washing.

Sometimes poor silver ores are roasted along with galena. The lead thus obtained contains the whole of the silver, which may then be separated by cupellation.

b. Amalgamation Process.—The amalgamation process formerly employed in Europe was conducted as follows: The finely-ground ore was mixed with common salt and roasted in a reverberatory furnace. By this means the silver, which was mostly present in the form of sulphide, was converted into chloride. The roasted ore was again ground very fine and then introduced, along with scrap iron and water, into casks which were made to revolve by machinery. The chloride was thus reduced to metallic silver:

$$\underset{\text{Argentic chloride.}}{2AgCl} + Fe = \underset{\text{Ferrous chloride.}}{FeCl_2} + Ag_2.$$

Mercury was then introduced into the revolving casks. The mercury combined with the silver to form a liquid amalgam, which was separated and subjected to distillation, when the mercury passed over and the silver remained in the retort. A modification of this proces is employed in Nevada. Some trouble is occasioned in this process by the tendency of the mercury to form minute globules, which, along with the silver contained in them, are lost in washing. This "flouring," or "sickening," as it is termed, which is due to the formation of a film of mercuric sulphide, may be prevented by the addition of about 2 per cent. of sodium to the mercury, the mercuric sulphide being thus reduced to metallic mercury, with formation of sodic sulphide.

The method of amalgamation employed in Mexico differs from the above, the scarcity of fuel in the silver-producing districts precluding the application of the roasting process. The ore is first ground very fine with water in a mill. The paste thus obtained is spread on a paved floor, and mixed with a small quantity of common salt, after which it is allowed to stand for a day. About 1 per cent. of a substance known to the miners as *magistral*—a mixture of crude ferric and cupric sulphates obtained by roasting copper pyrites—is added, and the whole is again thoroughly mixed. Mercury is now poured in, and the mixing is renewed. All these processes of incorporation are effected by the treading of blindfolded mules. The mercury is added in successive portions, at intervals of some days, during the working of the heap, the entire quantity of mercury employed being about six times the weight of the silver contained in the ore. The time required for working a heap varies from a fortnight to two months. At the end of the time the liquid amalgam, which contains all the silver, is separated from the earthy and other impurities by washing, and, after pressing in sacks to free it from the excess of mercury, is subjected to distillation.

The nature of the chemical changes which occur in the Mexican process is not thoroughly understood, but the action is supposed to take place as follows: The cupric sulphate undergoes double decomposition with the sodic chloride, yielding sodic sulphate and cupric chloride. The latter salt reacts with the argentic sulphide, converting it into argentic chloride:

$$\underset{\substack{\text{Cupric}\\\text{chloride.}}}{2\mathbf{Cu}Cl_2} + \underset{\substack{\text{Argentic}\\\text{sulphide.}}}{\mathbf{S}Ag_2} = \underset{\substack{\text{Cuprous}\\\text{chloride.}}}{'\mathbf{Cu}'_2Cl_2} + \underset{\substack{\text{Argentic}\\\text{chloride.}}}{2AgCl} + S.$$

The cuprous chloride thus formed dissolves in the sodic chloride present, and is thus enabled to act upon a fresh quantity of argentic sulphide:

$$\underset{\substack{\text{Cuprous}\\\text{chloride.}}}{'\mathbf{Cu}'_2Cl_2} + \underset{\substack{\text{Argentic}\\\text{sulphide.}}}{\mathbf{S}Ag_2} = \underset{\substack{\text{Cuprous}\\\text{sulphide.}}}{'\mathbf{Cu}'_2S''} + \underset{\substack{\text{Argentic}\\\text{chloride.}}}{2AgCl.}$$

The silver chloride held in solution by the sodic chloride is reduced by the metallic mercury, with formation of mercurous chloride:

$$\underset{\substack{\text{Argentic}\\\text{chloride.}}}{2AgCl} + 2Hg = \underset{\substack{\text{Mercurous}\\\text{chloride.}}}{'\mathbf{Hg}'_2Cl_2} + Ag_2.$$

The whole of this mercurous chloride is lost in washing, representing a loss of mercury equal to nearly twice the weight of the silver obtained.

c. Extraction in the Wet Way.—When argentiferous copper pyrites is roasted, the sulphides of iron, copper, and silver take up oxygen, and are converted into sulphates. By carefully regulating the temperature, a point may be reached at which the sulphates of iron and copper are decomposed, yielding insoluble oxides, whilst the more stable argentic sulphate remains unaltered, and may be obtained in solution afterwards by lixiviating the roasted mass with hot water. A small quantity of undecomposed copper salt goes into solution at the same time. The silver is precipitated from the solution by metallic copper. (Ziervogel.)

Another method consists in roasting the ore with common salt, so as to convert the silver into chloride, which is then extracted with a cold dilute solution of sodic thiosulphate. From this solution the silver is precipitated as sulphide by sodic sulphide. The argentic sulphide is reduced to metal by heating to a high temperature in a current of air. (Percy-Patera.)

The burnt pyrites obtained in the manufacture of sulphuric acid contains, in addition to copper, a small quantity of silver, amounting to about half an ounce to the ton. This small quantity may be profitably separated by adding to the tank-liquor obtained in the extraction of the copper (see Copper) a solution of kelp. In this way the silver, which is present in the tank-liquor in the form of chloride, and is kept in solution by the sodic chloride with which the burnt pyrites has been roasted, is precipitated as argentic iodide. A trace of gold, which is precipitated at the same time, is afterwards separated.

Preparation of Pure Silver.—In order to obtain pure silver advantage is taken of the insolubility of the chloride. Ordinary silver is dissolved in dilute nitric acid, when gold, if present, remains undissolved. The silver is precipitated from the filtered solution as chloride by hydrochloric acid. The washed and dried chloride is fused in a crucible with an excess of sodic carbonate. The silver collects as a regulus at the bottom of the crucible. Another method is to reduce the argentic chloride by laying it on a plate of zinc under dilute hydrochloric acid. The reduced silver is carefully washed with hydrochloric acid to free it from adhering traces of zinc, and is then dried. By this means it is obtained as a fine gray powder, devoid of metallic lustre. In this last form it is known as "molecular" silver (a misnomer, as it is very far from being in a state of molecular subdivision) and is used in organic research for acting upon organic compounds of the halogens.

Properties.—Silver has a white color, with a tinge of yellow, and possesses great lustre when polished. In the form in which it is obtained by the ignition of some organic silver salts, it is white like porcelain, owing to the roughness of its surface, and the consequent absence of metallic lustre. Of all the metals it is the best conductor of heat and electricity. It is a soft metal, standing between copper and gold in hardness. In malleability and ductility it is inferior only to gold; it can be beaten into leaf 0.00025 mm. in thickness, and can be drawn into wire of which 180 metres weigh 0.1 gram. In very thin films, as in the case when it

is deposited upon glass from ammoniacal solutions by means of reducing agents, it transmits blue light. It possesses great tenacity; the breaking weight for a wire 2 millimetres in diameter being 85 kilograms. Its specific gravity is 10.57. It crystallizes in regular octahedra. Native silver also occurs in dendritic forms. It fuses at 1040° C. (1904° F.), and may be distilled at a white heat by means of the oxyhydrogen blowpipe, a process which was employed by Stas in purifying silver for the purpose of determining its atomic weight. When melted in contact with air, pure silver absorbs about 22 times its volume of oxygen, which it again gives up at the moment of solidification. As the metal cools, the outer crust solidifies first, and the gas evolved from the interior then escapes through this crust in sudden bursts, carrying with it small particles of molten silver. This phenomenon is known as the "spitting" of silver. The presence of a small quantity of copper prevents the absorption of oxygen. Pure air, oxygen, and water are without action upon silver at all temperatures, but ozone oxidizes it superficially to peroxide.

Reactions.—1. Silver is blackened by sulphuretted hydrogen in presence of oxygen, argentic sulphide being formed. For this reason silver articles exposed to the atmosphere become discolored. Pure sulphuretted hydrogen, however, is without action upon silver at ordinary temperatures, and the metal may even be heated with an aqueous solution of sulphuretted hydrogen to 200° C. (392° F.) without blackening.

2. Silver is acted upon by hot concentrated sulphuric acid:

$$\underset{}{Ag_2} + \underset{\text{Sulphuric acid.}}{2\mathbf{S}O_2Ho_2} = \underset{\text{Argentic sulphate.}}{\mathbf{S}O_2Ago_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} + \underset{\text{Sulphurous anhydride.}}{\mathbf{S}O_2}.$$

3. Dilute nitric acid readily dissolves silver:

$$3Ag_2 + \underset{\text{Nitric acid.}}{8\mathbf{N}O_2Ho} = \underset{\text{Argentic nitrate.}}{6\mathbf{N}O_2Ago} + \underset{\text{Water.}}{4\mathbf{O}H_2} + \underset{\text{Nitric oxide.}}{2'\mathbf{N}''O}.$$

4. At a red heat silver decomposes hydrochloric acid:

$$Ag_2 + \underset{\text{Hydrochloric acid.}}{2HCl} = H_2 + \underset{\text{Argentic chloride.}}{2AgCl}.$$

Strong aqueous hydriodic acid dissolves silver, even at ordinary temperatures, with evolution of hydrogen and formation of argentic iodide.

Uses.—Pure silver is very little employed in the arts, as it is too soft to resist wear. In order to increase its hardness and tenacity, it is alloyed with a small proportion of copper, an addition which does not affect its color, and in this form it is employed for plate, ornaments, coinage, etc. *Standard silver* is an alloy of silver and copper of a given composition fixed by law, and this standard varies in different countries. In England the standard contains 92.5 per cent. of silver. In France, Germany, and Austria, the standard for coinage contains 90 per cent.

of silver, whilst there are other standards for plate and jeweller's work. What is termed the *fineness* of silver is the number of parts of silver per mille which the alloy contains; thus the English standard silver has a fineness of 925.

Pure silver is employed in the manufacture of various laboratory vessels; this metal, unlike glass and platinum, being capable of resisting the action of fused caustic alkalies.

Silver is also employed in electroplating. For this purpose the object to be silvered, which must possess a conducting surface, is made the negative electrode; the positive electrode consists of a plate of silver. The electrodes are immersed in a solution of argentic cyanide in an excess of potassic cyanide. The electrolytic silver is deposited as a coherent coating on the object to be silvered, and the cyanogen, liberated at the negative electrode, combines with the silver of the electrode to form argentic cyanide, which dissolves in the excess of potassic cyanide, so that the strength of the electrolytic solution remains constant. From silver solutions other than the above, the electrolytic silver is generally deposited in the form of a non-coherent powder.

The silvering of glass is effected by means of a mixture of an ammoniacal solution of silver with milk-sugar, or some other suitable organic reducing agent. The solution is contained in a flat shallow vessel, and the glass is suspended so that the surface to be silvered, which must previously have been thoroughly cleaned, may be in contact with the surface of the liquid. A bright coherent mirror of silver is thus deposited on the glass. Reflectors for astronomical telescopes are now extensively prepared by this method.

COMPOUNDS OF SILVER WITH THE HALOGENS.

ARGENTIC CHLORIDE, $AgCl$, occurs native, as *kerargyrite*, or *horn-silver*, in Mexico, Peru, and Chili, also in the Harz. Horn-silver crystallizes in forms belonging to the regular system, but more frequently occurs in wax-like, translucent masses. Its specific gravity varies from 5.3 to 5.4. Argentic chloride is obtained as a curdy precipitate by the addition of hydrochloric acid, or a soluble chloride, to the solution of a silver salt. When pure it is white; but under the influence of light it speedily assumes a violet tint, passing into black. The reason of this phenomenon, which is turned to account in photography, is not thoroughly understood, but the change is supposed to be due to the formation of a lower chloride, or to the liberation of metallic silver. The action is only superficial, and the quantity of chlorine evolved extremely small. Argentic chloride fuses at about 260° C. (500° F.) to a clear, yellow liquid, which solidifies to a translucent, horny, sectile mass. It is insoluble in water and dilute acids; slightly soluble in concentrated hydrochloric acid, and in concentrated solutions of the alkaline chlorides; readily soluble in ammonia, potassic cyanide, sodic thiosulphate, and in a concentrated solution of mercuric nitrate. On evaporation, the solutions in hydrochloric acid and in ammonia deposit the agentic chloride in octahedra. In contact with oxidizable metals, such as iron or zinc,

it is reduced, in presence of water, to metallic silver, the addition of a little acid favoring the reaction. The dry chloride absorbs gaseous ammonia to form the compound $2AgCl,3NH_3$, which parts with its ammonia at 37.7° C. (100° F.), and was employed by Faraday in the liquefaction of ammonia (p. 231). This compound is also obtained in large transparent rhombohedra, when a solution of argentic chloride in concentrated ammonia is allowed to stand in an imperfectly closed bottle.

Argentous chloride, Ag_4Cl_2, is obtained by treating argentous oxide (*q.v.*) with hydrochloric acid. It forms a black powder, which is decomposed by ammonia into metallic silver and argentic chloride, the latter dissolving in the ammonia. Nitric acid decomposes it in a similar manner, the silver in this case dissolving, whilst the chloride is left.

ARGENTIC BROMIDE, AgBr, occurs native as *bromargyrite* in Mexico and Chili, also at Huelgoet in Britanny. It generally forms concretions, but is also found crystallized. It may be prepared by precipitating solutions of silver salts with hydrobromic acid. At ordinary temperatures, hydrobromic acid converts argentic chloride into argentic bromide; at 700° C. (1292° F.), on the other hand, this reaction is reversed, and the bromide is converted by hydrochloric acid into chloride. Precipitated argentic bromide is a faint yellow substance, soluble with difficulty in dilute ammonia, readily soluble in concentrated ammonia. The dry bromide does not absorb ammonia; but a double compound with ammonia, corresponding to that of the chloride, is deposited from the ammoniacal solution. Argentic bromide fuses below a red heat. It is employed in photography in the preparation of "dry plates."

ARGENTIC IODIDE, AgI, is of very rare occurrence. It is found as *iodargyrite*, in Chili, Mexico, and Spain, in the form of thin hexagonal plates which are slightly elastic. It is obtained as an amorphous yellow precipitate when potassic iodide is added to the solution of a silver salt. Concentrated hydriodic acid dissolves metallic silver with evolution of hydrogen; from this solution lustrous laminæ of the formula AgI,HI are deposited on cooling; and these, on exposure to the air, are speedily decomposed, yielding argentic iodide. When the mother liquor from these crystals is exposed to the air, or when it is left in contact with excess of metallic silver, it deposits argentic iodide in hexagonal prisms. Argentic chloride and bromide are converted by hydriodic acid with violent reaction into the iodide; but above 700° C. (1292° F.) gaseous hydrochloric acide converts the iodide into chloride. Argentic iodide closely resembles the chloride and bromide, but differs from these in its almost perfect insolubility in concentrated ammonia, which, however, has the effect of turning it white. It is soluble in sodic thiosulphate, though not so readily as the chloride. It also dissolves in a concentrated solution of potassic iodide, the hot solution depositing on cooling acicular crystals of the formula AgI,HI; from this solution the iodide is precipitated by dilution with water. It fuses at a dull red heat, yielding a yellow liquid which becomes darker colored at a higher temperature, and on cooling solidifies to a yellow mass with a sp. gr. of 5.687. The sp. gr. of the precipitated iodide is 5.807, that of the crystallized variety 5.47–5.54. Fizeau has made the remarkable observa-

tion that between the temperatures of —10° and +70° C. (14° and 158° F.) argentic iodide contracts on heating and expands on cooling. Pure argentic iodide is not acted upon by light, but in presence of substances which are capable of combining with the liberated iodine it is slowly blackened. A slight admixture of argentic nitrate produces this effect. By exposure to light, however, even for a very short time, argentic iodide passes into a peculiar active condition, in which it possesses the property of immediately precipitating upon its surface black, finely-divided metallic silver from solutions of silver salts in presence of some reducing agent, such as pyrogallic acid. Upon this property the application of argentic iodide in photography depends, and the process of thus blackening the iodide is that of "developing" the photographic image. Dry argentic iodide absorbs gaseous ammonia, forming a white compound, $2AgI,\mathbf{N}H_3$, which, when exposed to the air, parts with ammonia, and is reconverted into yellow argentic iodide.

ARGENTIC FLUORIDE, AgF, is prepared by dissolving argentic oxide or argentic carbonate in hydrofluoric acid, and evaporating the solution. Argentic fluoride crystallizes either in colorless quadratic pyramids with 1 aq., or in prisms with 2 aq. It is deliquescent, and soluble in half its weight of water. It is not readily obtained in an anhydrous state When the compound $AgF,\mathbf{O}H_2$ is dried *in vacuo*, it undergoes partial decomposition, and a brownish-yellow earthy mass is formed, which, when heated with exclusion of air, may be fused, and on cooling solidifies to a black horny sectile mass. Unlike the chlorides of many of the metals, which in the fused state may be subjected to electrolysis, fused argentic fluoride conducts the electric current without undergoing decomposition. When heated in moist air it is reduced to the metallic state. The dry fluoride absorbs 844 times its volume of gaseous ammonia; at higher temperatures ammonia reduces it to metallic silver.

COMPOUNDS OF SILVER WITH OXYGEN.

The following three oxides of silver are known:

Argentous oxide (argentous quadrantoxide), .	OAg_4.
Argentic oxide, ...	$\mathbf{O}Ag_2$.
Argentic peroxide, ...	$\left\{\begin{array}{l}\mathbf{O}Ag\\ \mathbf{O}Ag\end{array}\right.$.

Argentous oxide, OAg_4, is obtained by heating argentic citrate in a current of hydrogen to 100° C.; on adding potassic hydrate to the solution of the bronze-colored mass thus obtained, argentous oxide is precipitated. It forms a black powder. Hydrochloric and hydrobromic acid convert it into argentous chloride and bromide. Oxy-acids decompose it, yielding an argentic salt and metallic silver. On heating, it breaks up into metallic silver and oxygen.

ARGENTIC OXIDE, $\mathbf{O}Ag_2$, is prepared by precipitating nitrate of silver with potassic hydrate or baryta-water, taking care to avoid the formation of carbonate; or by boiling freshly precipitated argentic chloride with a concentrated solution of potassic hydrate. When precipitated in the cold, it forms a dark-brown powder, which becomes black and

anhydrous on drying at 60° or 70° C. (140–158° F.). The recently precipitated and still moist *brown* oxide is in some respects more active in its combining properties than the dried *black* oxide; thus it absorbs carbonic anhydride from the air and substitutes hydroxyl for chlorine in the chlorides of organic ammonium bases; it therefore probably consists of the hydrate AgHo, which has not, however, been prepared in a state of purity. One part of argentic oxide dissolves in about 3000 parts of water, the solution possessing a marked alkaline reaction. The sp. gr. of the dry oxide is 7.25. In the dry state it acts as a powerful oxidizing agent, inflaming various oxidizable substances, such as sulphur, amorphous phosphorus, and the sulphides of arsenic and antimony, when triturated along with them. At a temperature of 250° C. (482° F.) it is decomposed into silver and oxygen, whilst in a current of hydrogen it undergoes reduction to metallic silver at 100° C. Argentic oxide is the salifiable oxide of silver:

$$\underset{\text{Argentic oxide.}}{\mathbf{O}Ag_2} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Argentic sulphate.}}{SO_2Ago_2} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

Strong ammonia converts argentic oxide into *fulminating silver* (*q.v.*).

Argentic peroxide, $\left\{\begin{matrix}\mathbf{O}Ag\\ \mathbf{O}Ag\end{matrix}\right.$.—This compound is formed by the action of ozone on finely divided silver. When a concentrated solution of argentic nitrate is submitted to electrolysis, argentic peroxide is deposited on the positive electrode. In like manner, in the electrolysis of acidulated water, if a silver plate be employed as positive electrode, the nascent oxygen combines with the silver, and the plate becomes coated with argentic peroxide. It forms minute black lustrous octahedra, which are frequently attached to each other. It is decomposed a little above 100° C. into oxygen and argentic oxide. Chlorine rapidly converts it at ordinary temperatures into argentic chloride and oxygen. Hydroxyl and argentic peroxide mutually reduce each other, oxygen being evolved from both substances:

$$\underset{\text{Argentic peroxide.}}{2\left\{\begin{matrix}\mathbf{O}Ag\\ \mathbf{O}Ag\end{matrix}\right.} + \underset{\text{Hydroxyl.}}{2\left\{\begin{matrix}\mathbf{O}H\\ \mathbf{O}H\end{matrix}\right.} = 2Ag_2 + \underset{\text{Water.}}{2\mathbf{O}H_2} + 3O_2.$$

Argentic peroxide possesses more powerful oxidizing properties than argentic oxide: when triturated with antimonious sulphide, the mixture deflagrates; sulphuretted hydrogen inflames in contact with the peroxide, the latter being converted into argentic sulphide; in aqueous ammonia the peroxide dissolves with evolution of nitrogen; when warmed in hydrogen it is reduced to metallic silver with a slight explosion. It seems to possess the properties of a weak base, forming salts which are stable only in solution with an excess of acid. Thus concentrated sulphuric acid dissolves it, forming a green liquid; but, on diluting with water, oxygen is evolved, and the solution contains argentic sulphate. With strong nitric acid it yields a brownish-red solution, which on dilu-

tion with water deposits the unchanged peroxide, the latter then redissolving in the dilute acid with evolution of oxygen and formation of argentic nitrate.

OXY-SALTS OF SILVER.

ARGENTIC NITRATE, $\mathbf{N}\mathrm{O_2Ago}$.—This salt is prepared by dissolving silver in dilute nitric acid, evaporating the solution, and allowing it to crystallize. It is thus obtained in colorless rhombic tabular crystals of sp. gr. 4.3, which fuse at 198° C. (388° F.), and solidify on cooling to a fibrous crystalline mass. Argentic nitrate is soluble in half its weight of water at ordinary temperatures, less soluble in nitric acid; soluble in four parts of boiling alcohol. The aqueous solution has a neutral reaction. Argentic nitrate has a disagreeable metallic taste, and is very poisonous. Applied to the flesh of animals, it acts as a powerful caustic, destroying the vitality of the part; the fused salt, cast into sticks, in which form it is known as *lunar caustic*, is employed in surgery for this purpose. The pure salt is not altered by exposure to light; but in contact with organic substances, light speedily blackens it. The hot concentrated solution dissolves argentic chloride slightly, argentic bromide more readily, and still more readily argentic iodide and cyandide. From these solutions the following compounds are deposited in needles on cooling:

$$\mathbf{N}\mathrm{O_2Ago,AgCl};\ \mathbf{N}\mathrm{O_2Ago,AgBr};\ 2\mathbf{N}\mathrm{O_2Ago,AgI};$$
$$\mathbf{N}\mathrm{O_2Ago,2Ag(CN)}.$$

These compounds are all decomposed by water with precipitation of the chloride, bromide, etc. Solid argentic nitrate absorbs gaseous ammonia, yielding a compound $\mathbf{N}\mathrm{O_2Ago,3NH_3}$.* A concentrated solution of argentic nitrate, when saturated with ammonia, deposits rhombic crystals of the formula $\mathbf{N}\mathrm{O_2Ago,2NH_3}$.† Argentic nitrate is extensively employed in photography. It also forms the basis of most of the indelible inks used for marking linen.

Argentic nitrite, $\mathbf{N}\mathrm{OAgo}$, is precipitated when concentrated solutions of potassic nitrite and argentic nitrate are mixed. It crystallizes in colorless or yellow prisms, which are sparingly soluble in cold, more readily soluble in warm water. At a temperature between 90° and 140° C. (162–284° F.) it is decomposed into metallic silver, nitric oxide, and argentic nitrate:

$$\underset{\text{Argentic nitrite.}}{4\mathbf{N}\mathrm{OAgo}} = \underset{\text{Argentic nitrate.}}{2\mathbf{N}\mathrm{O_2Ago}} + \underset{\text{Nitric oxide.}}{2'\mathbf{N}''\mathrm{O}} + \mathrm{Ag_2}.$$

Argentic chlorate, $\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ago}\end{matrix}\right.$, is obtained by dissolving argentic oxide in chloric acid. It is more readily prepared by passing chlorine into water in which argentic oxide is suspended; a mixture of chloride and hypochlorite (cf. p. 181) is thus formed, the latter decomposing in the dark at 60° C. (140° F.) into chloride and chlorate:

$$\underset{\text{Argentic hypochlorite.}}{3\mathrm{ClAgo}} = \underset{\text{Argentic chloride.}}{2\mathrm{AgCl}} + \underset{\text{Argentic chlorate.}}{\left\{\begin{matrix}\mathbf{O}\mathrm{Cl}\\ \mathbf{O}\mathrm{Ago}\end{matrix}\right.}$$

* $\mathbf{N}\mathrm{(NH_2)_2Ho_2(N^vAgH_3O)}$.

† $\mathbf{N}\mathrm{(NH_2)_2Ho_2Ago}$ or $\mathbf{N}\mathrm{O(NH_2)Ho(N^vAgH_3O)}$.

The liquid is filtered from the chloride and evaporated. Argentic chlorate crystallizes in white opaque quadratic prisms, soluble in 10 parts of cold water. It fuses at 230° C. (446° F.), and decomposes at 270° C. (518° F.) into oxygen and argentic chloride, a trace of chlorine being evolved at the same time. When rapidly heated it deflagrates. A mixture of argentic chlorate with sulphur detonates with great violence on friction.

Argentic bromate, $\left\{\begin{matrix}OBr\\OAgo\end{matrix}\right.$, and *argentic iodate,* $\left\{\begin{matrix}OI\\OAgo\end{matrix}\right.$, are obtained as sparingly soluble precipitates by the addition of solutions of the corresponding potash salts to a solution of argentic nitrate.

Argentic periodate.—When argentic nitrate is added to a neutral or slightly acid solution of an alkaline periodate, a dark-brown precipitate of the formula O_3IAgo,-$2OAg_2$ is obtained, which when heated to 200° C. (392° F.) is decomposed into argentic iodide, metallic silver, and oxygen. This salt dissolves in nitric acid, and deposits on evaporation orange-colored octahedra of *argentic metaperiodate,* O_3IAgo, which is decomposed by water into free periodic acid and an insoluble yellow salt of the formula $2O_3IAgo,OAg_2,3OH_2$.*

Argentic carbonate, $COAgo_2$, is precipitated when potassic or sodic carbonate is added to a solution of argentic nitrate. It forms a pale-yellow amorphous powder, insoluble in water. When exposed to light, or when warmed, it blackens. At a temperature of 100° C. it evolves carbonic anhydride, and is converted into argentic oxide.

ARGENTIC SULPHATE, SO_2Ago_2, is prepared by dissolving silver in hot concentrated sulphuric acid, or by precipitating a concentrated solution of argentic nitrate with sulphuric acid. It forms small lustrous crystals belonging to the rhombic system, of sp. gr. 5.4. It is soluble in about 200 parts of cold and in 68.35 parts of boiling water; more readily soluble in dilute sulphuric or nitric acid. At a dark red heat it fuses without decomposition; at a higher temperature it breaks up into metallic silver, oxygen, and sulphurous and sulphuric anhydrides. The solid salt absorbs two molecules of gaseous ammonia, forming the compound $SO_2Ago_2,2NH_3 = SO_2(N^vAgH_3O)_2$. A solution of the salt in warm aqueous ammonia deposits on cooling quadratic crystals of the compound $SO_2Ago_2,4NH_3 = S(NH_2)_2Ho_2(N^vAgH_3O_2)$.—*Hydric argentic sulphate,* SO_2HoAgo, crystallizes in pale yellow prisms from a solution of the normal salt in less than three parts of sulphuric acid. If more sulphuric acid be employed, double compounds of the acid salt with sulphuric acid are obtained.

Argentic sulphite, $SOAgo_2$, is prepared by dissolving argentic oxide in sulphurous acid, or by precipitating argentic nitrate with an alkaline sulphite or with sulphurous acid, avoiding an excess of the precipitant. It crystallizes in white shining needles, or forms a curdy precipitate, only slightly soluble in water. When exposed to light, it blackens. At a temperature of 100° C. it is decomposed into sulphurous anhydride, argentic sulphide, and metallic silver:

$$\underset{\text{Argentic sulphite.}}{2SOAgo_2} = \underset{\text{Argentic sulphate.}}{SO_2Ago_2} + \underset{\text{Sulphurous anhydride.}}{SO_2} + Ag_2.$$

Argentic dithionate, $\left\{\begin{matrix}SO_2Ago\\SO_2Ago\end{matrix}\right.$, OH_2, is prepared by dissolving argentic carbonate in the aqueous acid. It crystallizes in rhombic prisms.

Argentic thiosulphate (*Argentic hyposulphite*), $SO_2AgoAgs$.—When a dilute solution

* On the formulation of these compounds on the basis of *heptaic* iodine, *e.g.*, $IOAgo_5$, IO_3Ago, and $IOHo_3Ago_2$, see p. 305.

of argentic nitrate is added to an excess of a solution of sodic thiosulphate, a gray precipitate is formed, consisting of a mixture of argentic sulphide with argentic thiosulphate. The thoroughly washed precipitate is treated with ammonia which extracts the thiosulphate. On carefully neutralizing the ammoniacal solution with nitric acid the argentic thiosulphate is reprecipitated as a white powder, sparingly soluble in water. It must be quickly dried by pressure, as in the moist state it readily decomposes into argentic sulphide and sulphuric acid:

$$\underset{\text{Argentic thiosulphate.}}{\mathbf{S}O_2AgoAgs} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Argentic sulphide.}}{\mathbf{S}Ag_2} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2}.$$

Sodic argentic thiosulphate, $\mathbf{S}O_2NaoAgs,2\mathbf{O}H_2$, is obtained by gradually adding, with constant stirring, a solution of sodic thiosulphate to a solution of argentic nitrate till the precipitate no longer redissolves. On adding alcohol to the filtrate, the double salt separates in lustrous laminæ.

ARGENTIC PHOSPHATE:

a. Argentic orthophosphate, $\mathbf{P}OAgo_3$, is precipitated when argentic nitrate is added to a solution of any normal or monohydric alkaline phosphate, nitric acid being liberated in the latter case. It forms a yellow amorphous precipitate, insoluble in water, readily soluble in nitric acid and in ammonia. It becomes dark-colored when exposed to light. When heated it assumes a deep orange-red color, and fuses at a strong red heat without decomposition.—*Hydric diargentic orthophosphate*, $\mathbf{P}OHoAgo_2$, is deposited as a white crystalline powder when ether is added to a solution of the normal salt in excess of phosphoric acid.

b. Argentic pyrophosphate, $\mathbf{P}_2O_3Ago_4$, is obtained as a white precipitate when argentic nitrate is added to solutions of either normal or acid pyrophosphates of the alkali metals. It is insoluble in water, readily soluble in nitric acid or ammonia. It fuses without decomposition below redness, yielding a dark brown liquid which solidifies on cooling to a radio-crystalline mass. Under the influence of light it turns red.

c. Argentic metaphosphate, $\mathbf{P}O_2Ago$.—The various modifications of metaphosphoric acid yield corresponding silver salts. Thus, if argentic nitrate be added to a solution of the vitreous sodic metaphosphate, an amorphous white precipitate of the silver salt is obtained; whereas crystallizable sodic trimetaphosphate yields, when so treated, well-formed crystals of *argentic trimetaphosphate*, $\mathbf{P}_3O_6Ago_3,\mathbf{O}H_2$.

Argentic arsenate, $\mathbf{As}OAgo_3$, is obtained as a reddish-brown amorphous precipitate when an alkaline arsenate is added to the solution of a silver salt. The same salt may be obtained as a dark-red crystalline powder by precipitating a boiling solution of argentic nitrate with a concentrated solution of arsenic acid. It is insoluble in water, readily soluble in nitric acid and in ammonia. When heated it fuses, yielding a reddish-brown glass on cooling.

Argentic arsenite, $\mathbf{As}Ago_3$, is prepared by cautiously adding ammonia to a mixed solution of argentic nitrate and arsenious acid as long as a precipitate is produced. It forms a yellow precipitate, readily soluble in nitric acid and in ammonia. On heating, it decomposes into arsenious anhydride, argentic arsenate, and metallic silver:

$$\underset{\text{Argentic arsenite.}}{5\mathbf{As}Ago_3} = \underset{\text{Argentic arsenate.}}{3\mathbf{As}OAgo_3} + \underset{\text{Arsenious anhydride.}}{\mathbf{As}_2O_3} + 3Ag_2.$$

By boiling with sodic hydrate it is decomposed into arsenic anhydride, which dissolves with formation of sodic arsenate, and metallic silver, the latter being mixed with argentous oxide (OAg_4).

COMPOUNDS OF SILVER WITH SULPHUR.

ARGENTIC SULPHIDE, SAg_2.—This compound occurs native as *silver glance* or *argentite* in blackish-gray regular crystals with a metallic lustre. It has a sp. gr. of from 7.196 to 7.356. Artificial crystals of argentite are obtained when silver is heated in a current of sulphuretted hydrogen, and the same substance may be prepared as a crystalline mass by fusing together silver and sulphur. A black amorphous precipitate of argentic sulphide is formed when sulphuretted hydrogen is passed into solutions of silver salts. Argentic sulphide is insoluble in water, soluble with decomposition in strong nitric acid, insoluble in ammonia. When heated in air, avoiding too high a temperature, it is oxidized to argentic sulphate. Cupric chloride in presence of sodic chloride converts it into argentic chloride (see Mexican Amalgamation Process).

SULPHO-SALTS OF SILVER.

Argentic sulpharsenite, $AsAgs_3$, occurs native as *proustite* or *light red silver ore*, in red translucent rhombohedral crystals. It generally contains more or less antimony, which is present in isomorphous replacement of a portion of the arsenic.

Argentic sulphantimonite, $SbAgs_3$, occurs as *pyrargyrite* or *dark red silver ore*, in rhombohedral crystals, isomorphous with the preceding. It varies in color from dark red to grayish-black, is opaque, and possesses metallic lustre.

COMPOUNDS OF SILVER WITH NITROGEN AND PHOSPHORUS.

Fulminating silver.—This compound is formed when freshly precipitated argentic oxide is dissolved in strong ammonia, and the solution is evaporated with the aid of a gentle warmth. It forms black crystals, which when dry explode violently on the slightest touch, and even when moist may be made to explode by shaking the liquid in which they are immersed. Owing to the dangerous character of this compound its composition has not been ascertained with certainty. It is possibly *argentic amide*, $NAgH_2$.

Argentic phosphide is formed when phosphorus is added to molten silver, or when argentic phosphate is fused with charcoal. It is thus obtained as a dark gray mass, which, when strongly heated, parts with a portion of its phosphorus. This compound has not been obtained of constant composition.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF SILVER.—The salts of silver with colorless acids are colorless. The soluble salts are neutral to test-paper, have an acrid metallic taste, and act as violent irritant poisons. From solutions of silver salts *caustic alkalies* precipitate brown argentic oxide. *Ammonia* also precipitates the oxide, which is soluble however in an excess of the precipitant. *Sulphuretted hydrogen* gives a black precipitate of argentic sulphide, insoluble in ammonic sulphide, soluble in hot nitric acid. The *hydracids* precipitate the corresponding haloid compounds of silver (p. 452). *Hydrocyanic acid* and *potassic cyanide* give a curdy precipitate of argentic cyanide (AgCy) soluble in excess of potassic cyanide. Argentic cyanide is decomposed on ignition, leaving a residue of metallic silver. *Copper, zinc, iron*, and other oxidizable metals, further, *sulphurous acid*

and *ferrous sulphate*, precipitate metallic silver from the solutions of its salts. Insoluble compounds of silver, when heated with sodic carbonate on charcoal before the blowpipe, are reduced to metallic silver. The silver compounds give no flame spectrum; but the spark spectrum exhibits two characteristic bright lines in the green.

CHAPTER XXXIII.

DYAD ELEMENTS.

SECTION II.

BARIUM, Ba.

Atomic weight = 137. *Probable molecular weight* = 137. *Sp. gr. between* 4.0 *and* 5.0. *Atomicity* ″. *Evidence of atomicity:*

Baric chloride, ...	$Ba''Cl_2$.
Baric hydrate, ...	$Ba''Ho_2$.
Baric oxide, ...	$Ba''O$.

History.—Metallic barium was first prepared by Davy in 1808.

Occurrence.—Barium is never found native. It occurs abundantly as sulphate in the mineral *heavy-spar* and as carbonate in *witherite.* In many calcium minerals it sometimes replaces a portion of the calcium, with which it is isomorphous. Traces of it are found in various mineral waters and in sea-water.

Preparation.—Barium is not reduced from its oxide, hydrate, or carbonate, by heating with charcoal. It may be obtained by the following methods:

1. By the electrolysis of the fused chloride (see Preparation of Lithium, p. 436). The barium is thus obtained in the form of a metallic powder.

2. By electrolyzing moistened baric hydrate, carbonate, nitrate, or chloride, the negative electrode being formed of mercury. A liquid amalgam of barium is thus obtained, which may be freed from the excess of mercury by pressing through a cloth. The solid amalgam which remains is only slowly oxidized by exposure to the air. On subjecting it to distillation mercury passes over and metallic barium remains in the retort as a porous mass.

3. By acting with sodium amalgam upon a hot concentrated solution of baric chloride, barium amalgam is obtained, which is further treated as above.

4. Barium amalgam is also obtained by passing the vapor of potassium or sodium over baric oxide or chloride strongly heated in an iron tube, and extracting the mass with mercury.

Properties.—Barium is a pale yellow metal. Its fusing-point appears to be higher than that of cast-iron. It is rapidly oxidized by expo-

sure to the air, and decomposes water at ordinary temperatures like sodium:

$$\underset{}{Ba} + \underset{\text{Water.}}{2OH_2} = H_2 + \underset{\text{Baric hydrate.}}{BaHo_2}.$$

COMPOUNDS OF BARIUM WITH THE HALOGENS.

Baric chloride, $BaCl_2,OH_2$, may be prepared either from the native carbonate or from the native sulphate. The carbonate is dissolved in hydrochloric acid, and the liquid is digested with an excess of the carbonate in order to precipitate iron and other foreign metals that are present. The addition of a small quantity of baric hydrate facilitates this precipitation. The filtered liquid is acidified with hydrochloric acid and evaporated. In order to prepare baric chloride from the native sulphate, this mineral is ground to a fine powder and then strongly heated with calcic chloride, limestone, and coal. The following reactions occur:

$$\underset{\substack{\text{Baric}\\\text{sulphate.}}}{SO_2Bao''} + 4C = \underset{\substack{\text{Baric}\\\text{sulphide.}}}{BaS''} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{4CO}.$$

$$\underset{\substack{\text{Baric}\\\text{sulphide.}}}{BaS''} + \underset{\substack{\text{Calcic}\\\text{chloride.}}}{CaCl_2} = \underset{\substack{\text{Baric}\\\text{chloride.}}}{BaCl_2} + \underset{\substack{\text{Calcic}\\\text{sulphide.}}}{CaS''}.$$

The calcic sulphide unites with the calcic oxide present to form an insoluble calcic oxysulphide, which remains behind when the baric chloride is extracted with water.—Baric chloride crystallizes in colorless lustrous rhombic tables, with 2 aq., permanent in air. The sp. gr. of the crystallized salt is 3.05. It has an unpleasant bitter taste, and, like all the soluble salts of barium, is very poisonous. The anhydrous salt is soluble in 3 times its weight of water at 10° C. (50° F.), and in about $1\frac{2}{3}$ times its weight of water at 100° C. It is almost insoluble in concentrated hydrochloric and nitric acids; in the dilute acids it is soluble, but less freely than in water. Absolute alcohol does not dissolve it. When heated above 100° C., the crystallized salt parts with its water of crystallization, and is converted into a white powder fusible at a red heat. When fused in air a small quantity of the salt is converted into baric oxide with evolution of chlorine; when heated in a current of steam hydrochloric acid is given off below the fusing-point of the salt, and baric hydrate is formed.—Baric chloride is chiefly used in the preparation of the pigment *permanent white*, which consists of artificial baric sulphate.

Baric bromide, $BaBr_2,2OH_2$, is prepared by dissolving baric carbonate in hydrobromic acid. The following method is the most convenient: 12.5 parts of bromine and 1 part of amorphous phosphorus are brought together under water. As soon as the color of the bromine has disappeared the liquid, which now contains hydrobromic and phosphoric acid, is neutralized with baric carbonate, rendered alkaline with baryta water, filtered from the insoluble baric phosphate, and evaporated to the point of crys-

tallization. Baric bromide closely resembles the chloride, but is soluble in absolute alcohol.

Baric iodide, $BaI_2,2OH_2$, is prepared like he bromide, substituting iodine for bromine. It forms large, colorless, rhombic crystals, which are very deliquescent, and are soluble in alcohol. When exposed to the air it assumes a reddish tint, owing to the liberation of iodine. It may be heated in a closed vessel without decomposition, but when heated in air the whole of the iodine is expelled, and baric oxide is formed.

Baric fluoride, BaF_2, is obtained by neutralizing hydrofluoric acid with baric carbonate or hydrate, or by precipitating a concentrated solution of baric nitrate with potassic or sodic fluoride. It forms a white granular crystalline powder, sparingly soluble in water, readily soluble in nitric, hydrochloric, and hydrofluoric acids.

Baric silicofluoride, $SiBaF_6$, is precipitated as a white crystalline powder, when hydrofluosilicic acid is added to the solution of a barium salt. It is almost insoluble in water, requiring 3500 parts of cold, and 1200 parts of boiling water for its solution; totally insoluble in alcohol.

COMPOUNDS OF BARIUM WITH OXYGEN.

Baric oxide (*baryta*), ... BaO. $Ba{=}O$.

Baric peroxide, ... $Ba\left.\begin{matrix}O\\O\end{matrix}\right\}$ $Ba\begin{matrix}\diagup O\\ \,|\\ \diagdown O\end{matrix}$.

Baric oxide, BaO.—This is the oxide which is formed by the combustion of the metal in air. It may be prepared by heating the nitrate, gently at first, in order to avoid frothing, and afterwards to bright redness. The frothing may also be prevented by mixing the nitrate with its own weight of baric sulphate, the presence of the insoluble sulphate in the product not being objectionable for many purposes to which the baric oxide may be put, for instance in the preparation of baric hydrate. The carbonate may also be converted into baric oxide by heating to a very high temperature, but the whole of the carbonic anhydride can be expelled only with difficulty; however, by mixing the carbonate with carbon, or with some substance which yields carbon when heated, such as tar or resin, the conversion into baric oxide is greatly facilitated, carbonic oxide being evolved, thus:

$$\underset{\text{Baric carbonate.}}{COBao''} + C = \underset{\text{Baric oxide.}}{BaO} + \underset{\text{Carbonic oxide.}}{2CO}.$$

Much of the baryta employed in sugar refining (p. 464) was prepared by this method. Baric oxide is a grayish-white, porous, friable mass, of sp. gr. 4.73. It is fusible in the flame of the oxyhydrogen blowpipe. It slakes with water, forming baric hydrate, the combination taking place with such energy that, if an excess of water is avoided, the mass becomes incandescent.

Baric peroxide, $Ba\left.\begin{matrix}O\\O\end{matrix}\right\}$, is formed when baric oxide is heated to low redness in oxygen or air. Baric hydrate is also converted into the peroxide under these circumstances, but less readily, inasmuch as it fuses below the temperature at which the absorption of oxygen occurs. The product obtained by these means is not pure, a portion of the baric

oxide or hydrate escaping conversion. It is also contaminated with iron, silica, and other matters derived from the vessels in which it has been prepared. In order to obtain the substance in a state of purity, the finely-powdered crude product is added in small portions at a time to an excess of dilute hydrochloric acid, any considerable rise of temperature being avoided. The crude peroxide dissolves, with formation of baric chloride and hydroxyl (cf. p. 175). To the solution, after filtering from insoluble matters, baryta water is carefully added until the silica and ferric oxide, along with a small quantity of hydrated baric peroxide regenerated by the action of the hydroxyl upon the baric hydrate, are precipitated:

$$\underset{\text{Hydroxyl.}}{\left\{\begin{matrix}\mathbf{O}\mathrm{H}\\ \mathbf{O}\mathrm{H}\end{matrix}\right.} + \underset{\text{Baric hydrate.}}{\mathbf{Ba}\mathrm{Ho}_2} = \underset{\text{Baric peroxide.}}{\left.\mathbf{Ba}\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}} + \underset{\text{Water.}}{2\mathbf{O}\mathrm{H}_2}.$$

This liquid is again filtered, and then supersaturated with baryta. In this way the whole of the remaining hydroxyl regenerates baric peroxide, which is precipitated in minute prisms or laminæ of the formula $\left.\mathbf{Ba}\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\},8\mathbf{O}\mathrm{H}_2$. In the moist condition this aquate may be preserved for any length of time in closed vessels, and forms a convenient source of hydroxyl. By drying at 130° C., or at ordinary temperatures *in vacuo*, it is converted into anhydrous baric peroxide.—Baric peroxide forms a white impalpable powder, insoluble in water, but forming with it the aquate $\left.\mathbf{Ba}\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\},8\mathbf{O}\mathrm{H}_2$. It fuses at a bright red heat, and is decomposed into oxygen and baric oxide. Heated with steam it evolves oxygen at the same temperature at which the peroxide is formed, and is converted into baric hydrate. Dilute acids dissolve it with formation of a barium salt and hydroxyl; with concentrated sulphuric acid it forms baric sulphate, whilst oxygen mixed with traces of ozone and hydroxyl is evolved. When heated in a current of sulphurous anhydride it becomes incandescent, and is converted into baric sulphate:

$$\underset{\substack{\text{Sulphurous}\\ \text{anhydride.}}}{\mathbf{S}\mathrm{O}_2} + \underset{\substack{\text{Baric}\\ \text{peroxide.}}}{\left\{\begin{matrix}\mathbf{O}\\ \mathbf{O}\end{matrix}\right.\mathrm{Ba}} = \underset{\substack{\text{Baric}\\ \text{sulphate.}}}{\mathbf{S}\mathrm{O}_2\left(\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\mathrm{Ba}\right)''}.$$

COMPOUND OF BARIUM WITH HYDROXYL.

Baric hydrate, $\mathbf{Ba}\mathrm{Ho}_2$.—This compound is formed, with great evolution of heat, by the direct union of baric oxide with water. A hot concentrated solution of equivalent quantities of baric nitrate and sodic hydrate deposits, on cooling, crystals of baric hydrate. Potassic hydrate may be substituted for sodic hydrate in this reaction; but ammonia does not precipitate baric hydrate from solutions of barium salts. On a large scale, baric hydrate is prepared as follows: By heating

powdered heavy-spar with carbon a crude baric sulphide is obtained. Moist carbonic anhydride is passed over the heated sulphide, converting it into carbonate:

$$\underset{\text{Baric sulphide.}}{\mathbf{BaS''}} + \underset{\text{Carbonic anhydride.}}{\mathbf{CO_2}} + \underset{\text{Water.}}{\mathbf{OH_2}} = \underset{\text{Baric carbonate.}}{\mathbf{COBao''}} + \underset{\text{Sulphuretted hydrogen.}}{\mathbf{SH_2}}.$$

Superheated steam is then passed over the heated carbonate, which parts with carbonic anhydride and forms baric hydrate:

$$\underset{\text{Baric carbonate.}}{\mathbf{COBao''}} + \underset{\text{Water.}}{\mathbf{OH_2}} = \underset{\text{Baric hydrate.}}{\mathbf{BaHo_2}} + \underset{\text{Carbonic anhydride.}}{\mathbf{CO_2}}.$$

—Baric hydrate crystallizes from water in large four-sided prisms or plates, of the formula $\mathbf{BaHo_2,8OH_2}$, which are soluble in 20 parts of water at ordinary temperatures, and in 3 parts at 100° C. The solution of the hydrate, generally known as *baryta water*, is much used in chemical analysis, particularly in the determination of carbonic anhydride, which it rapidly absorbs, with formation of insoluble baric carbonate. The crystals of the hydrate are efflorescent, and when exposed *in vacuo* over sulphuric acid, give off the greater part of their water of crystallization, leaving a white powder of the formula $\mathbf{BaHo_2,OH_2}$. When heated, the whole of the water of crystallization is expelled, and the hydrate fuses at a red heat, solidifying on cooling to a crystalline mass. It cannot be converted into baric oxide by the action of heat alone. Heated in a current of air, it is converted into baric peroxide with elimination of water:

$$\underset{\text{Baric hydrate.}}{\mathbf{BaHo_2}} + \mathrm{O} = \underset{\text{Baric peroxide.}}{\mathbf{Ba}\left.\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right\}} + \underset{\text{Water.}}{\mathbf{OH_2}}.$$

Baric hydrate was extensively employed in sugar-refining for separating crystallizable sugar from molasses. It forms with cane sugar an insoluble compound of the formula $C_{12}H_{22}O_{11}BaO$, which when suspended in water and treated with carbonic anhydride is decomposed, yielding insoluble baric carbonate and sugar, the latter dissolving. Strontic hydrate, which, unlike the barium compound, is not poisonous, has of late been substituted for baric hydrate in the sugar industry.

OXY-SALTS OF BARIUM.

BARIC NITRATE, $\begin{matrix}\mathbf{NO_2}\\ \mathbf{NO_2}\end{matrix}\mathrm{Bao''}$.—This salt is prepared by dissolving the carbonate or the crude sulphide (p. 461) in dilute nitric acid. It crystallizes in colorless, lustrous, regular octahedra, of sp. gr. 3.2. It is soluble in 12 parts of cold, in 3 parts of boiling water; almost insoluble in concentrated nitric acid; insoluble in absolute alcohol. It fuses at

597° C. (1107° F.). Heated to redness it decomposes, giving off oxygen, nitrogen, and nitric peroxide, whilst a residue of pure baric oxide remains. It is largely employed in pyrotechny for the preparation of green fire.

Baric nitrite, $\begin{matrix}NO\\NO\end{matrix}Bao'',OH_2$.—Baric nitrate is moderately heated so as to convert it into nitrite; carbonic anhydride is then passed into the solution of the fused salt to precipitate any baryta that may have been formed; an excess of alcohol is added to precipitate unaltered nitrate, and the filtered solution is evaporated to the crystallizing point. It is most readily prepared pure by adding baric chloride to a boiling solution of argentic nitrite, and filtering from the argentic chloride. It forms colorless prisms, very soluble in water.

Baric chlorate, $\left\{\begin{matrix}OCl\\O\\O\\OCl\end{matrix}\right. Bao'',OH_2$, is formed when chlorine is passed into a hot solution of baric hydrate, but its separation from the chloride which is formed at the same time is a matter of difficulty. It is best prepared by neutralizing a solution of chloric acid with baric carbonate and evaporating to the crystallizing point. It crystallizes in colorless monoclinic prisms, with 1 aq., soluble in 4 parts of cold, in less than 1 part of boiling water.

Baric perchlorate, $\left\{\begin{matrix}OCl\\O\\O\\O\\O\\OCl\end{matrix}\right. Bao'',4OH_2$, is prepared by neutralizing perchloric acid with baric hydrate or carbonate. It crystallizes in long deliquescent prisms, readily soluble in water and in alcohol.

BARIC CARBONATE, $COBao''$.—This salt occurs abundantly in nature as *witherite*. It may be prepared by pouring a solution of baric chloride or nitrate into an excess of a solution of ammonic carbonate, and washing the precipitate with hot water. The native carbonate forms lustrous crystals belonging to the rhombic system, of sp. gr. 4.29–4.35; that prepared by precipitation is a dense white powder. It is insoluble in pure water; slightly soluble in water containing carbonic anhydride, probably with formation of an unstable acid carbonate. It fuses at a white heat, giving off carbonic anhydride very slowly; but it is more readily decomposed by heat in presence of carbon, or when steam is passed over it (pp. 462 and 463). The artificial carbonate is employed in chemical analysis. Witherite is used in the preparation of the other salts of barium and as a rat poison.

BARIC SULPHATE, SO_2Bao'', occurs in large quantities as *heavy-spar*, sometimes forming distinct veins. It is frequently found in large rhombic crystals. The sp. gr. of the mineral varies between 4.3 and 4.72. By precipitating solutions of barium salts with dilute sulphuric acid, baric sulphate is obtained as a white impalpable powder of sp. gr. 4.53. It is insoluble in water, slightly soluble in dilute acids. When freshly precipitated it is readily soluble in concentrated sulphuric acid at 100° C., the solution depositing, on cooling, lustrous prisms of *dihydric baric sulphate*, $\left\{\begin{matrix}SO_2Ho\\Bao''\\SO_2Ho\end{matrix}\right.$. If the acid solution is exposed to the air it absorbs moisture, and deposits silky needles of a salt having the

formula $\begin{cases} SO_2Ho \\ Bao'' \\ SO_2Ho \end{cases},2OH_2$. Both these salts are decomposed by water, yielding sulphuric acid and the neutral salt. Artificial baric sulphate is used as a pigment, under the name of *permanent white* or *blanc fixe.* The finely ground mineral is also employed for this purpose, but is too crystalline and transparent, and hence lacks "body."

Baric pyrosulphate, $\begin{cases} SO_2 \urcorner \\ O \quad Bao'' \\ SO_2 \lrcorner \end{cases}$.—Precipitated baric sulphate dissolves in fuming sulphuric acid, and the solution, on heating to 150° C. (302° F.), deposits lustrous granular crystals of this salt. It decomposes at a dull read heat, without previously fusing.

Baric sulphite, $SOBao''$, is obtained as a white crystalline precipitate by the addition of an alkaline sulphite to the solution of a barium salt. It crystallizes from its solution in warm aqueous sulphurous acid in six-sided prisms. When heated in air it is converted into sulphate; in closed vessels it yields, when heated, a mixture of sulphate and sulphide.

$$\underset{\text{Baric sulphite.}}{4SOBao''} = \underset{\text{Baric sulphate.}}{3SO_2Bao''} + \underset{\text{Baric sulphide.}}{BaS.}$$

Baric dithionate, $\begin{cases} SO_2 \\ SO_2 \end{cases} Bao'',2OH_2$.—Preparation, see p. 278. This salt crystallizes in large, lustrous, monoclinic crystals, soluble in 4 parts of water at 18° C. (64° F.), in 1.1 part at 100° C. The solution may be boiled without undergoing decomposition; but when boiled with hydrochloric acid, it evolves sulphurous anhydride, and baric sulphate is precipitated. In like manner, when the dry salt is ignited it breaks up into sulphurous anhydride and baric sulphate:

$$\underset{\text{Baric dithionate.}}{\begin{cases} SO_2 \\ SO_2 \end{cases} Bao''} = \underset{\text{Baric sulphate.}}{SO_2Bao''} + \underset{\text{Sulphurous anhydride.}}{SO_2.}$$

Baric dithionate is employed in the preparation of the other dithionates.

Baric thiosulphate, $SO_2\left(\begin{matrix} O \\ S'' \end{matrix}Ba\right)'',OH_2$, is obtained as a sparingly soluble crystalline precipitate when sodic thiosulphate is added to a solution of baric chloride.

Baric orthophosphate, $\begin{matrix} POBao'' \\ POBao'' \end{matrix}Bao'',OH_2$, is prepared by adding hydric disodic orthophosphate to a solution of baric chloride rendered strongly alkaline with ammonia. It forms a white precipitate, insoluble in water, soluble in dilute nitric and hydrochloric acids.—*Hydric baric orthophosphate,* $POHoBao''$, is precipitated when hydric disodic orthophosphate is added to neutral solutions of barium salts. It is a white crystalline powder, slightly soluble in water, readily soluble in dilute acids.—*Tetrahydric baric orthophosphate,* $\begin{matrix} POHo_2 \\ POHo_2 \end{matrix}Bao''$, is obtained by evaporating a solution of the monacid salt in phosphoric acid. It forms colorless crystals, apparently triclinic, with an acid reaction. It is soluble without decomposition in a small quantity of water; excess of water precipitates the monacid salt, whilst free phosphoric acid remains in solution.

COMPOUNDS OF BARIUM WITH SULPHUR.

Baric sulphide, **Ba**S″, is obtained by passing sulphuretted hydrogen over the heated oxide. It is prepared on a large scale by heating heavy-spar with carbon. The materials must be thoroughly incorporated; otherwise, owing to their infusibility, the action will be only partial. The finely ground heavy-spar is mixed with powdered bituminous coal; the latter fuses, yielding by its decomposition a carbon which permeates the entire mass of the sulphate, and insures its complete reduction. The sulphide obtained by this method is always contaminated with the excess of carbon, and is only used for the preparation of the various salts of barium (see p. 464). Baric sulphide forms a white mass which, when exposed to the air, absorbs water, oxygen, and carbonic anhydride, and is gradually converted into a mixture of sulphate and carbonate. Water dissolves it, but the solution contains a mixture of hydrate and sulphhydrate:

$$\underset{\text{Baric sulphide.}}{2\mathbf{Ba}S''} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Baric hydrate.}}{\mathbf{Ba}Ho_2} + \underset{\text{Baric sulphhydrate.}}{\mathbf{Ba}Hs_2}.$$

The so-called *Bolognian phosphorus* is a sulphide of barium prepared by heating 5 parts of precipitated baric sulphate with 1 part of carbon. It must be sealed up while still hot in glass tubes. After exposure to sunlight, or to any other light rich in chemically active rays, it displays in the dark a brilliant orange-colored light, and retains this phosphorescent property, though with gradually diminishing intensity, for some time. The luminosity may be renewed indefinitely often by fresh exposure to light. The sulphides of calcium and strontium are also phosphorescent, and emit a green, blue, violet, or red light, according to the mode of preparation. These various sulphides are at present manufactured under the name of *luminous paints*, and are employed for coating clock-faces, match-boxes, and other objects which it is desired to render luminous in the dark. It is necessary, in order that these paints may preserve their efficiency unimpaired, that they should be protected from the moisture of the air. This is effected by a transparent coating of glass or varnish.

Baric tetrasulphide, $BaS_4.\mathbf{O}H_2$, is obtained in pale-red rhombic prisms by boiling a solution of baric sulphhydrate with sulphur and allowing the solution to cool. It is readily soluble in water.

Various other polysulphides of barium have been prepared. They are unstable compounds, which in contact with water are decomposed with formation of the tetrasulphide.

COMPOUND OF BARIUM WITH HYDROSULPHYL.

Baric sulphhydrate, $\mathbf{Ba}Hs_2$, is formed along with baric hydrate by the action of water on baric sulphide (*supra*). It may be prepared pure by saturating a solution of baric hydrate with sulphuretted hydrogen. It forms colorless very soluble crystals, containing water of crystallization. When heated with exclusion of air, it parts with the water of crystallization, and at a higher temperature evolves sulphuretted hydrogen, whilst baric sulphide remains.

General Properties and Reactions of the Compounds of Barium.—The salts of barium with colorless acids are colorless. The soluble salts have a bitter taste and are poisonous. Baric chloride and baric nitrate are both insoluble in absolute alcohol. *Sulphuric acid* and soluble *sulphates* produce in solutions of barium salts a white precipitate of baric sulphate insoluble in dilute acids. *Alkaline carbonates* precipitate baric carbonate. *Hydrofluosilicic acid* gives a colorless crystalline precipitate of baric silicofluoride. *Potassic chromate* and *potassic dichromate* precipitate yellow baric chromate, insoluble in acetic acid. Barium salts color the non-luminous flame yellowish-green. Of the numerous lines in the complex spectrum, the two green lines, Baα and Baβ, are the brighest.

STRONTIUM, Sr.

Atomic weight = 87.5. *Probable molecular weight* = 87.5. *Sp. gr.* 2.5. *Fuses at a red heat. Atomicity* ''. *Evidence of atomicity:*

Strontic chloride, ...	$Sr''Cl_2$.
Strontic hydrate, ...	$Sr''Ho_2$.
Strontic oxide, ...	$Sr''O$.

History.—Hope showed in 1792 that the mineral strontianite contained a new earth. The metal was first isolated by Davy in 1808.

Occurrence.—Strontium occurs as carbonate in *strontianite*, and as sulphate in *celestine*. Traces of it are present as carbonate in many kinds of limestone, marble, and chalk. It also occurs in minute quantities as chloride and sulphate in brine-springs, mineral waters, and sea-water.

Preparation.—Strontium is most readily prepared by the electrolysis of the fused chloride. By this means it is obtained in coherent pieces sometimes weighing half a gram.—By heating a saturated solution of strontic chloride with sodium-amalgam, an amalgam of strontium is formed, from which the mercury may be expelled by heating.

Properties.—Strontium is a yellow malleable metal. It undergoes rapid oxidation on exposure to the air, burns with a brilliant light when heated, and decomposes water at ordinary temperatures.

COMPOUNDS OF STRONTIUM WITH THE HALOGENS.

Strontic chloride, $SrCl_2,6OH_2$, is prepared like the barium salt (p. 461). It crystallizes in deliquescent hexagonal needles or prisms of sp. gr. 1.603, readily soluble in water, soluble also in alcohol. When heated, it parts with its water of crystallization, leaving the anhydrous salt in the form of a white powder, which fuses at a higher temperature. The anhydrous chloride absorbs dry ammonia, forming the compound $SrCl_2,8NH_3$.

Strontic bromide, $SrBr_2,6OH_2$, is prepared like the barium salt (p. 461). It resembles strontic chloride in its properties.

Strontic iodide, $SrI_2,7OH_2$, is prepared like the barium salt (p. 462). It crystallizes in six-sided plates, and is very soluble. When heated in air it parts with iodine, and is converted into strontic oxide.

Strontic fluoride, SrF_2, is prepared like the barium salt (p. 462), which it also resembles in its properties.

Strontic silicofluoride, $SiSrF_6,2OH_2$, is obtained by neutralizing hydrofluosilicic acid with strontic carbonate, and evaporating to the crystallizing point. It forms monoclinic crystals, readily soluble in water.

COMPOUNDS OF STRONTIUM WITH OXYGEN AND HYDROXYL.

Strontic oxide, *Strontia*, . .	$\mathbf{Sr}O$.	$Sr{=}O$.
Strontic peroxide, ...	$\mathbf{Sr}\left.\begin{matrix}O\\O\end{matrix}\right\}$.	$Sr\left\langle\begin{matrix}O\\\mid\\O\end{matrix}\right.$.
Strontic hydrate, ...	$\mathbf{Sr}Ho_2$.	$H{-}O{-}Sr{-}O{-}H$.

Strontic oxide, $\mathbf{Sr}O$.—This compound is prepared like baric oxide (p. 462). It forms a grayish-white, infusible, porous mass resembling baric oxide in its properties and reactions. It combines with water to form *strontic hydrate*, $\mathbf{Sr}Ho_2$.

Strontic peroxide, $\mathbf{Sr}\left.\begin{matrix}O\\O\end{matrix}\right\}$, separates in crystalline laminæ with 8 aq. when a solution of hydroxyl is added to an excess of a solution of strontic hydrate. In dry air or when heated to 130° C. it parts with its water of crystallization, leaving the pure peroxide as a white powder. This, when heated to redness, evolves oxygen, and is converted into strontic oxide, without however first fusing, as in the case of baric peroxide.

Strontic hydrate, $\mathbf{Sr}Ho_2,8OH_2$, is formed as above by the action of water upon strontic oxide. It resembles baric hydrate, but is somewhat less soluble in water, and, when strongly heated, parts with water and is reconverted into the oxide.

OXY-SALTS OF STRONTIUM.

Strontic nitrate, $\begin{matrix}\mathbf{N}O_2\\\mathbf{N}O_2\end{matrix}Sro''$.—This salt is prepared by dissolving the native carbonate in nitric acid. It crystallizes from hot concentrated solutions on cooling in anhydrous octahedra of sp. gr. 2.96, and from cold dilute solutions in large monoclinic prisms with 4 aq., which effloresce when exposed to the air. It is soluble in twice its weight of water at 15° C. (59° F.), and in its own weight of water at 100° C., but is insoluble in alcohol.—Strontic nitrate is employed in pyrotechny in the manufacture of red fire.

Strontic chlorate, $\left\{\begin{matrix}OCl\\O\\O\\OCl\end{matrix}\right.Sro'',5OH_2$, is prepared by dissolving the carbonate in chloric acid. It forms deliquescent crystals, very soluble in water.

STRONTIC CARBONATE, $COSro''$, occurs native as *strontianite* in rhombic crystals, isomorphous with those of *arragonite*, one of the forms of native calcic carbonate. It is obtained as a white insoluble precipitate when an alkaline carbonate is added to the solution of a strontium salt.

STRONTIC SULPHATE, SO_2Sro'', occurs native as *celestine* in rhombic crystals, or in fibrous masses, generally of a light blue color, from which property the name of the mineral is derived. Sulphuric acid precipitates strontic sulphate as a white powder from solutions of strontium salts. The precipitate is generally crystalline, and has a specific gravity of 3.07. It is slightly soluble in cold, less soluble in hot water; the presence of acids increases the solubility. The aqueous solution produces in solutions of barium salts a strong turbidity. It fuses at a bright red heat, yielding a vitreous mass on cooling. When digested with solutions of alkaline carbonates in the cold, or with hot mixed solutions of 2 parts of potassic carbonate with 1 part of potassic sulphate, it is completely converted into strontic carbonate, a property sharply distinguishing it from baric sulphate, which under these circumstances undergoes no change. With concentrated sulphuric acid, strontic sulphate behaves like baric sulphate (p. 465), yielding an acid salt which is decomposed by excess of water into the normal salt and free sulphuric acid.

Strontic sulphite, $SOSro''$.—Prepared like the barium salt (p. 466), which it also resembles.

Strontic dithionate, $\left\{\begin{matrix} SO_2 \\ SO_2 \end{matrix}\right. Sro'',OH_2$.—Prepared like the barium salt (p. 466). Very soluble hexagonal crystals.

Strontic thiosulphate, $SO_2\left(\begin{matrix} O \\ S'' \end{matrix}Sr\right)'',5OH_2$, is prepared by dissolving sulphur in a solution of strontic hydrate, and then saturating with sulphurous anhydride (cf. p. 277). It forms lustrous monoclinic crystals, readily soluble in water.

The *orthophosphates* of strontium correspond closely, both in properties and mode of preparation, with those of barium.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF STRONTIUM.—The salts of strontium closely resemble those of barium. Those formed with colorless acids are colorless. The soluble salts have a bitter taste, but are not poisonous. Strontic chloride is soluble in absolute alcohol; strontic nitrate is insoluble in this solvent. From solutions of strontium salts *alkaline carbonates* precipitate strontic carbonate. Strontic sulphate is slightly soluble: a solution of this salt produces in solutions of barium salts a precipitate of baric sulphate. *Hydrofluosilicic acid* and soluble *chromates* give no precipitate with strontium salts. Strontium compounds color the non-luminous flame a brilliant red. The flame-spectrum is complex: the lines $Sr\alpha$ in the orange, $Sr\beta$ and $Sr\gamma$ in the red, and $Sr\delta$ in the blue are the brightest.

CALCIUM, Ca.

Atomic weight = 40. *Probable molecular weight* = 40. *Sp. gr.* 1.578.
Atomicity''. Evidence of atomicity:

Calcic chloride, ...	$Ca''Cl_2$.
Calcic hydrate, ...	$Ca''Ho_2$.
Calcic oxide, ...	$Ca''O$.

History.—Lime, and its use in the preparation of mortar, have been known from the earliest times. The metal was first isolated by Davy in 1808.

Occurrence.—The compounds of calcium occur in nature in enormous quantities and widely diffused. As carbonate it occurs under a great variety of forms, as *calc-spar*, *marble*, *limestone*, etc. Calcic sulphate also occurs in large quantities: either as the anhydrous sulphate (SO_2Cao'') in *anhydrite*, or as tetrahydric calcic sulphate (SHo_4Cao'') in *gypsum*. The compound silicates of calcium with other metals form a series of minerals which are among the proximate constituents of the various rocks. From the rocks and soils it is extracted by the water which percolates through them, so that spring and river water are rarely free from salts of calcium, chiefly the carbonate and sulphate. Calcium is necessary to the existence of most forms of organized matter: in combination with various organic acids it occurs in plants, whilst the bones of animals contain calcic phosphate and carbonate. Spectrum analysis has demonstrated the presence of calcium in the sun and in some of the fixed stars.

Preparation.—Davy prepared impure calcium in the form of a metallic powder by electrolyzing calcic chloride with mercury as a negative electrode, and heating the calcium amalgam so as to expel the mercury. It is most readily prepared by the electrolysis of the fused chloride. Pieces of pure calcium weighing as much as four grams may be thus obtained. Another method consists in heating calcic iodide with sodium. Calcium is also very readily obtained by heating to redness a mixture of 3 parts of fused calcic chloride, 4 parts of zinc, and 1 part of sodium, when an alloy of zinc and calcium, containing from 10 to 16 per cent. of the latter metal, collects at the bottom of the crucible. This alloy is transferred to a crucible made of gas coke, which is packed inside a larger Hessian crucible, and the whole is heated to a temperature sufficiently high to volatilize the zinc. The fused calcium, which remains as a button at the bottom of the coke crucible, is not so pure as that obtained by electrolysis.

Properties.—Calcium is a yellow metal, lustrous when freshly cut. It is about as hard as gold, and is very malleable. It does not oxidize readily in dry air, but in moist air it speedily becomes coated with hydrate, the action gradually extending throughout the whole mass. It decomposes water at ordinary temperatures with violent evolution of hydrogen. Dilute nitric acid dissolves it, the reaction taking place with such violence that the metal sometimes inflames. Concentrated

nitric acid, on the other hand, is without action upon calcium at ordinary temperatures, a freshly-cut surface of the metal remaining bright in contact with the acid; and it is not until the temperature has been raised to near the boiling-point of the acid that oxidation takes place. This phenomenon is analogous to that of the so-called "passive state" of iron (*q.v.*). When heated in air calcium burns, emitting a brilliant yellow light.

COMPOUNDS OF CALCIUM WITH THE HALOGENS.

CALCIC CHLORIDE, $CaCl_2,6OH_2$, occurs in sea-water, river-water, and spring-water. It is obtained as a by-product in several manufacturing operations, as for example in the preparation of ammonia (p. 231), of potassic chlorate (p. 182), etc. In order to prepare pure calcic chloride from a crude manufacturing product, or from the product obtained by dissolving marble in hydrochloric acid, chlorine-water is added to the solution until the smell of the chlorine can be distinctly perceived. By this means any manganous or ferrous compounds which may be present are oxidized. Milk of lime is added until the solution is alkaline, the liquid is heated, and the precipitate, consisting of ferric, manganic, and aluminic hydrates, together with the excess of lime, is filtered off. The solution is acidified with pure hydrochloric acid and evaporated either to the crystallizing point or to dryness, according to the purpose for which the salt is required.—Calcic chloride crystallizes in large transparent hexagonal prisms of the formula

$$CaCl_2,6OH_2,$$

isomorphous with those of strontic chloride, soluble in half their weight of water at 0° C. (32° F.) and in one-quarter of their weight at 16° C. (60.8° F.). The crystals fuse at 29° C. (84.2° F.) in their water of crystallization, and are therefore soluble in hot water in all proportions. They deliquesce when exposed to air, yielding an oily liquid. Concentrated solutions of calcic chloride boil at a much higher temperature than pure water, and are employed in the laboratory as baths, when constant temperatures above 100° C. (212° F.) are required. *In vacuo* over sulphuric acid the crystallized salt parts with 4 aq.; the remaining 2 aq. can be expelled only above 200° C. (392° F.). The anhydrous salt thus obtained is a white porous mass which, when heated to redness, fuses and, if the fusion be performed with free access of air, acquires an alkaline reaction, owing to the conversion of a small quantity of the chloride into oxide. On cooling, the fused salt solidifies to a colorless, translucent, crystalline mass, of sp. gr. 2.205. The anhydrous salt, both in the porous and in the fused form, absorbs water with great avidity, and is therefore used for drying gases and liquids. The porous form is best suited for drying gases, on account of the greater surface which it exposes; whilst, in the case of liquids, fused calcic chloride is preferred, as the porous variety would absorb too much of the liquid to be dried. The anhydrous salt dissolves in water

with evolution of heat. It is also soluble in absolute alcohol, forming with it a crystallized compound, which is decomposed by water. The aquate,

$$CaCl_2,6OH_2,$$

dissolves in water with great absorption of heat, and when mixed with snow in the proportion of 1.44 parts of the former to 1 of the latter, produces a depression of temperature equal to —54.9° C. (—66.8 F.) (Hammerl).—When a solution of calcic chloride is boiled with calcic hydrate and filtered hot, it deposits on cooling white acicular crystals of *dicalcic oxychlorhydrate*, $\left\{\begin{matrix}CaCl\\O\\CaHo\end{matrix}\right.,7OH_2$.—Anhydrous calcic chloride absorbs gaseous ammonia with great avidity, forming the compound $CaCl_2,8NH_3$ as a white powder, which, by the action of water or of heat, or by exposure to the air, is resolved into its constituents. Owing to this property of absorbing ammonia, calcic chloride cannot be employed in drying that gas.

Calcic bromide, $CaBr_2$.—Prepared like baric bromide (p. 461). Resembles calcic chloride in its properties.

Calcic iodide, CaI_2.—Prepared like baric iodide (p. 462). Resembles calcic chloride in most of its properties. When heated in contact with air it parts with the whole of its iodine, yielding calcic oxide.

CALCIC FLUORIDE, CaF_2, occurs abundantly in nature as *fluor-spar*, sometimes massive, sometimes crystallized in octahedra, cubes, and other forms belonging to the regular system. When pure it is colorless, but the mineral generally exhibits a variety of tints—blue, violet, green, red, etc.—due to the presence of impurities. It also occurs in the ashes of plants, in bones, and in the enamel of the teeth. It is formed as a granular powder when calcic hydrate or carbonate is digested with aqueous hydrofluoric acid, and as a gelatinous precipitate when a soluble fluoride is added to the solution of a calcium salt. It can be artificially obtained in microscopic octahedra by heating the precipitated salt with very dilute hydrochloric acid for several hours in sealed tubes to 240° C. (464° F.), or by heating calcic silicofluoride with a solution of calcic chloride to 250° C. (482° F.). It dissolves in 2000 parts of water at 15° C. (59° F.), and is somewhat more soluble in dilute acids. Fluor-spar phosphoresces in the dark when heated. At a red heat it fuses without decomposition. Fluor-spar is employed as a flux in various metallurgical operations. The brilliantly colored varieties are manufactured into ornamental vases, dishes, and other articles.

Calcic silicofluoride, $SiCaF_6,2OH_2$.—Prepared by dissolving calcic carbonate in hydrofluosilicic acid and evaporating to the crystallizing point. Soluble, monoclinic crystals.

COMPOUNDS OF CALCIUM WITH OXYGEN.

Calcic oxide, . .	**CaO.**	$Ca{=}O$.
Calcic peroxide, .	$\mathbf{Ca}\left.\begin{matrix}O\\O\end{matrix}\right\}$.	$Ca\left\langle\begin{matrix}O\\\vert\\O\end{matrix}\right.$.

Calcic oxide (*Quicklime*), **CaO**.—This substance is prepared on a large scale by burning limestone or chalk (impure calcic carbonate) in kilns. In the continuous process of lime-burning, now frequently employed, the limestone mixed with coal is introduced at the top of the furnace, and the quicklime withdrawn at the lower part. Calcic oxide may be obtained on a small scale by strongly heating pure marble or calc-spar in a crucible with a perforated bottom, this arrangement being adopted to allow the furnace gases to pass over the heated carbonate, and thus assist the decomposition by carrying off the carbonic anhydride as fast as it is evolved. In an atmosphere of carbonic anhydride calcic carbonate may be heated to whiteness without change. Calcic oxide forms a white amorphous mass, of sp. gr. 3.08. It is infusible at the highest temperatures which can be artificially produced. When heated in the oxyhydrogen flame, it emits an intense light, this arrangement constituting the so-called lime-light. When exposed to the air, it absorbs water and carbonic anhydride, and is converted into carbonate. It combines with water to form calcic hydrate: when large pieces of lime are moistened with water, they speedily become very hot, give off steam, and crumble to a white powder—a process which is known as the *slaking* of the lime. Quicklime is employed in the laboratory for drying gases and liquids.

Calcic peroxide, $\mathbf{Ca}\left.\begin{matrix}O\\O\end{matrix}\right\}$.—Prepared like strontic peroxide (p. 469), which it closely resembles.

COMPOUND OF CALCIUM WITH HYDROXYL.

Calcic hydrate (*slaked lime*), $\mathbf{Ca}Ho_2$, is obtained as above by slaking lime with water. It forms a white amorphous powder, of sp. gr. 2.078. It is sparingly soluble in water, and less soluble in hot than in cold water, one part of the hydrate dissolving in 600 to 700 parts of water, at ordinary temperatures, and requiring twice that quantity at 100° C. (212° F.). The solution, which is known as lime-water, has an alkaline reaction, and absorbs carbonic anhydride from the air, forming a precipitate of insoluble calcic carbonate; when evaporated *in vacuo*, it deposits small tabular or prismatic crystals of calcic hydrate. When lime-water is prepared from ordinary lime, it is best to treat the slaked lime several times with water in order to remove traces of baric and strontic hydrates and soluble salts of the alkalies, with which it is usually contaminated, before using it to make the solution. *Milk of lime* is calcic hydrate mixed with a quantity of water insufficient for its

solution, and thus forming a thick milky liquid. At a red heat calcic hydrate is decomposed into calcic oxide and water. When made into a paste with water and exposed to the air, it gradually solidifies to a hard mass, and the action is more rapid when sand is mixed with the lime. Such a mixture of one part of freshly slaked lime, made into a paste with water, and three or four parts of sharp sand, constitutes ordinary *building mortar.* The hardening or *setting* of mortar is due to the formation of calcic carbonate and not, as was formerly supposed, to a gradual combination of the sand with the lime to form calcic silicate. The sand merely acts by its mass in preventing a too great contraction of the calcic hydrate whilst setting. *Hydraulic mortar* or *Roman cement,* which has the property of setting under water, is prepared from a limestone containing silica or clay (aluminic silicate). This limestone requires care in burning: if the temperature be permitted to rise too high the lime is vitrified and will not slake. The lime thus prepared consists of a mixture of calcic and aluminic silicates, and combines with water, without sensible elevation of temperature, to form a hard mass upon which water has no further action. *Portland cement* is a hydraulic mortar prepared from chalk and clay found in the valley of the Medway. Lime is also used in tanning for removing hair and wool from skins; in the preparation of the caustic alkalies (p. 415); in sugar refining, for precipitating acids and nitrogeneous substances from the juice; and as a manure, in order to render clay soils lighter.

OXY-SALTS OF CALCIUM.

CALCIC NITRATE, $\begin{matrix}NO_2\\NO_2\end{matrix}Cao'',4OH_2$, occurs as an efflorescence on moist walls, particularly in stables and other places where there is much organic refuse. It is contained in fertile soil, and in great quantity in the soil of nitre plantations (p. 214). It may be prepared by dissolving the carbonate in nitric acid. Calcic nitrate is deposited, by slow evaporation from concentrated aqueous solutions, in monoclinic crystals with 4 aq. The anhydrous salt is a white deliquescent mass. It is soluble also in alcohol.

Calcic nitrite, $\begin{matrix}NO\\NO\end{matrix}Cao'',OH_2$.—Prepared like the barium salt (p. 464). Colorless, very soluble prisms.

Calcic chlorate, $\left\{\begin{matrix}OCl\\O\\O\\OCl\end{matrix}\right.Cao'',2OH_2$.—Prepared like the barium salt (p. 465. See also preparation of potassic chlorate, p. 182). Very soluble, deliquescent crystals.

CALCIC HYPOCHLORITE, $\begin{matrix}OCl\\OCl\end{matrix}Ca$, is difficult to prepare in a state of purity. It is formed, along with calcic chloride, when chlorine is passed into cold milk of lime:

$$\underset{\text{Calcic hydrate.}}{2CaHo_2} + 2Cl_2 = \underset{\text{Calcic hypochlorite.}}{\begin{matrix}OCl\\OCl\end{matrix}Ca} + \underset{\text{Calcic chloride.}}{CaCl_2} + \underset{\text{Water.}}{2OH_2}.$$

Bleaching powder or *chloride of lime*, the substance obtained by the action of chlorine upon dry slaked lime, was formerly considered to be a mixture of calcic hypochlorite with calcic chloride; but most chemists at present regard it as calcic chloro-hypochlorite, $\mathbf{Ca}(OCl)Cl$:

$$\underset{\text{Calcic hydrate.}}{\mathbf{Ca}Ho_2} + Cl_2 = \underset{\text{Calcic chloro-hypochlorite.}}{\mathbf{Ca}(OCl)Cl} + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

The dry slaked lime is spread in a layer on the floor of a long, low-roofed chamber, of lead or flagstones, into which the chlorine is passed. In practice it is not found possible to effect the absorption of the entire quantity of chlorine corresponding to the above equation: the commercial product contains from 20 to 35 per cent. of *available chlorine*—that is, chlorine which is liberated as such when the bleaching powder is treated with sulphuric or hydrochloric acid:

$$\underset{\text{Calcic chloro-hypochlorite.}}{\mathbf{Ca}(OCl)Cl} + \underset{\text{Sulphuric acid.}}{\mathbf{S}O_2Ho_2} = \underset{\text{Calcic sulphate.}}{\mathbf{S}O_2Cao''} + \underset{\text{Water.}}{\mathbf{O}H_2} + Cl_2.$$

Water converts calcic chloro-hypochlorite into a mixture of calcic chloride and calcic hypochlorite:

$$\underset{\text{Calcic chloro-hypochlorite.}}{2\mathbf{Ca}(OCl)Cl} = \underset{\text{Calcic chloride.}}{\mathbf{Ca}Cl_2} + \underset{\text{Calcic hypochlorite.}}{\mathbf{Ca}(OCl)_2}.$$

A solution of bleaching powder, filtered from the unattacked calcic hydrate which the commercial product always contains, and evaporated *in vacuo*, deposits crystals of calcic hypochlorite of the formula $\mathbf{Ca}(OCl)_2,4\mathbf{O}H_2$. Owing to its instability, this salt is difficult to obtain pure. Bleaching powder is a white powder with a faint odor of hypochlorous acid. When heated to redness, it evolves oxygen with formation of calcic chloride. Concentrated solutions also give off oxygen on boiling, and even dilute solutions may be made to part with the whole of their oxygen by boiling them with a small quantity of the hydrates of cobalt, nickel, manganese, iron, etc. (p. 161). In closed vessels it undergoes decomposition from causes not understood, this decomposition occasionally taking place with such violence as to give rise to explosions. Its chief employment is in bleaching. In this operation the cloth is first dipped in a dilute solution of bleaching powder and afterwards passed through very dilute sulphuric or hydrochloric acid. The hypochlorous acid is thus liberated in presence of hydrochloric acid—the latter being either added as such or set free from the calcic chloride by the sulphuric acid—and these two acids mutually decompose each other with liberation of chlorine (p. 180), which in the moist state destroys the organic coloring matter, and thus bleaches the cloth. Chloride of lime is also used as a disinfectant.

Similar bleaching compounds are formed by the action of chlorine upon baric and strontic hydrates.

CALCIC CARBONATE, $\mathbf{C}OCao''$.—This compound occurs abundantly and widely distributed in nature, in the crystallized form as *calcite* or *calc-spar* and *arragonite*, in crystalline masses as *marble*, and in an amorphous or crypto-crystalline condition as *limestone* and *chalk;* also in coral, shells of molluscs, egg-shells and bone-ash. It is an important constituent of soils and is contained in nearly all spring and river water. It is precipitated from solutions of calcium salts by the addition of an alkaline carbonate. Calcic carbonate is dimorphous, occurring in rhombohedral crystals of sp. gr. 2.70 to 2.75 as calcite, and in rhombic prisms of sp. gr. 2.92 to 3.28 as arragonite. It is precipitated from hot solutions as a fine crystalline powder displaying the forms of arragonite; from cold solutions it is deposited as an amorphous powder which gradually becomes crystalline, assuming the forms of calcite. It is insoluble in pure water, somewhat soluble in water containing carbonic anhydride, giving rise to what is known as the *temporary hardness of water*. The solubility is due to the formation of *dihydric calcic carbonate*, $\begin{matrix}\mathbf{C}OHo\\ \mathbf{C}OHo\end{matrix}Cao''$, which, however, can exist only in solution. On boiling the solution this salt decomposes into carbonic anhydride, which is expelled, water, and insoluble calcic carbonate; and the temporary hardness is thus removed. The removal of the temporary hardness may also be effected by adding lime-water as long as a precipitate of calcic carbonate is formed. The solution of dihydric calcic dicarbonate also parts with its carbonic anhydride on exposure to the air, depositing calcic carbonate. In this way the various calcareous deposits, such as calcareous tufa, stalactites, etc., from natural waters are formed. Sometimes the solution yields six-sided prisms of the formula $\mathbf{C}OCao'',5\mathbf{O}H_2$, which part with their water of crystallization at 19° C. Calcic carbonate is more readily decomposed at a red heat into oxide and carbonic anhydride than baric and strontic carbonates (see preparation of calcic oxide, p. 474).

CALCIC SULPHATE, $\mathbf{S}O_2Cao''$.—The anhydrous salt occurs as the mineral *anhydrite*, either in rhombic crystals, or in crystallo-granular masses. More commonly, however, calcic sulphate is found in the hydrated condition as *tetrahydric calcic sulphate* ($\mathbf{S}Ho_4Cao'' = \mathbf{S}O_2Cao'',$-$2\mathbf{O}H_2$) in the mineral *gypsum*, either in monoclinic prisms as *selenite*, or in fibrous satiny masses as *satin-spar*, or in the crystallo-granular form as *crystalline gypsum* or *alabaster*. It occurs in the soil and in most natural waters. The tetrahydric sulphate is precipitated as a crystalline powder from solutions of calcium salts, if not too dilute, by the addition of sulphuric acid. Gypsum is sparingly soluble in water, requiring 487 parts of water at 0° C. (32° F.) and 433 parts of water at 35° C. (95° F.) for solution. Above 35° C. its solubility again decreases, one part of the salt requiring more than 500 parts of water at 100° C. (212° F.) to dissolve it. It is much more soluble in dilute acids and in solutions of ammoniacal salts and of sodic chloride than in pure water. Solutions of sodic thiosulphate dissolve it very readily. It parts with most of its water of hydration between 100° C. (212° F.) and 120° C. (248° F.), forming *burnt gypsum* or *plaster of Paris*. If the salt which has been dehydrated at this temperature is mixed with

water, it combines rapidly with the water to form the tetrahydric sulphate, and if the water has been added only in quantity sufficient to form a thin paste, the whole speedily solidifies to a white mass, at the same time undergoing slight expansion. Upon these properties the use of plaster of Paris in taking casts is based, the property of expanding during solidification causing it to fill the crevices of the mould and thus reproduce all the details of a design. Ordinary plaster of Paris is much more soluble in water than gypsum, requiring for solution only 82 parts of water at 22° C. (71.6° F.). A solution prepared by shaking the salt with water at the ordinary temperature and quickly filtering, soon deposits crystals of gypsum. If gypsum is heated to above 200° C. (392° F.) it parts with the whole of its water of hydration, yielding the anhydrous sulphate; but in this condition it combines only very slowly with water, and does not solidify. Gypsum which has been thus overheated is said to be *dead burnt.* If it is dehydrated at a temperature of 500° C. (932° F.), it also takes up water very slowly, the process requiring several weeks for completion, but the product of re-hydration is a hard mass, denser than ordinary gypsum, and translucent like alabaster; and this mass may be converted into ordinary plaster of Paris by dehydrating at a low temperature. At a red heat anhydrous calcic sulphate fuses, solidifying to a crystalline mass. A solution of an alkaline carbonate converts gypsum at ordinary temperatures into calcic carbonate. When heated with concentrated sulphuric acid to 100° C. (212° F.), it is converted into a porous crystalline mass of *dihydric calcic sulphate,* $\begin{matrix}SO_2Ho\\SO_2Ho\end{matrix}Cao''$, whilst part goes into solution, and, on cooling, separates in flat prisms with a silky lustre, having the formula $\begin{matrix}SO_2Ho\\SO_2Ho\end{matrix}Cao'',2SO_2Ho_2$. Both these salts are decomposed by water into gypsum and sulphuric acid.

Calcic dipotassic sulphate, $\begin{matrix}SO_2Ko\\SO_2Ko\end{matrix}Cao'',OH_2$.—This double salt occurs native in monoclinic crystals as *syngenite.* If equal parts of plaster of Paris and anhydrous potassic sulphate be mixed with less than their weight of water, the whole suddenly solidifies. By employing a larger proportion of water a mixture may be obtained which yields casts exhibiting a polished surface.

Calcic disodic sulphate, $\begin{matrix}SO_2Nao\\SO_2Nao\end{matrix}Cao''$, occurs native as *glauberite.* An aquate of the formula $\begin{matrix}SO_2Nao\\SO_2Nao\end{matrix}Cao'',2OH_2$ is obtained in acicular crystals by heating a mixture of plaster of Paris and sodic sulphate with water.

Calcic sulphite, $SOCao'',2OH_2$.—Prepared like the barium salt (p. 466), which it also resembles.

Calcic dithionate, $\left\{\begin{matrix}SO_2\\SO_2\end{matrix}\right.Cao'',4OH_2$.—Prepared like the barium salt (p. 278). Very soluble, hexagonal crystals.

Calcic thiosulphate, $SO_2\left(\begin{matrix}O\\S''\end{matrix}Ca\right)'',6OH_2$.—Prepared like the strontium salt (p. 470). Triclinic prisms, readily soluble in water.

CALCIC ORTHOPHOSPHATE, $\begin{matrix}POCao''\\POCao''\end{matrix}Cao''$, occurs as *osteolite* and *sombrerite.* When crystallized with 2 aq. it forms the mineral *ornithite.*

As a double phosphate and fluoride of the formula $\mathbf{P}_3\mathrm{O}_3\mathrm{Cao}''_4\left(\begin{smallmatrix}\mathrm{O}\\ \mathrm{F}\end{smallmatrix}\mathrm{Ca}''\right)$, in which a portion of the fluorine is sometimes isomorphously replaced by chlorine, it occurs in hexagonal crystals as the mineral *apatite*. *Phosphorite* is an impure and massive apatite. Calcic orthophosphate is contained in the soil, from which it is taken up by plants, and thus finds its way into the bodies of animals. It forms the chief constituents of the bones and teeth of animals, of the scales of fishes, etc. Coprolites, supposed to be the fossilized excrement of extinct animals, consist for the most part of calcic orthophosphate. Calcic orthophosphate is obtained as a white gelatinous precipitate by adding ordinary (monohydric) sodic phosphate in excess to a solution of calcic chloride, previously rendered alkaline with ammonia. It is almost insoluble in water, but is decomposed by continued boiling into an insoluble basic salt and an acid salt which dissolves. It is moderately soluble in solutions of various salts and in water containing carbonic anhydride. By means of this last property, the calcic phosphate contained in the soil is rendered soluble, so as to be assimilable by plants. It is readily soluble in hydrochloric, nitric, and acetic acids, and is reprecipitated by ammonia from the acid solutions.—*Hydric calcic orthophosphate*,

$$\mathbf{P}\mathrm{OHoCao}'',2\mathbf{O}\mathrm{H}_2,$$

occurs native as *brushite*. It is obtained as a crystalline precipitate on adding calcic chloride to an acetic acid solution of ordinary sodic phosphate.—*Tetrahydric calcic orthophosphate*,

$$\begin{matrix}\mathbf{P}\mathrm{OHo}_2\\ \mathbf{P}\mathrm{OHo}_2\end{matrix}\mathrm{Cao}'',\mathbf{O}\mathrm{H}_2,$$

is prepared by evaporating a solution of either of the preceding salts in aqueous phosphoric acid. It forms rhombic tables or laminæ. A small quantity of water converts it into insoluble monohydric phosphate and free phosphoric acid, but the precipitate disappears if left in contact with the liquid and stirred with it from time to time. If shaken up with a hundred times its weight of water, tetrahydric calcic phosphate speedily dissolves, but on boiling the solution, the monohydric phosphate separates as an anhydrous precipitate, and the liquid contains phosphoric acid. Sodic acetate also precipitates the monohydric phosphate from the solution. The tetrahydric phosphate gives off its water of crystallization at 100° C. (212° F.); when heated to 200° C. (392° F.) it parts with the elements of water, and is converted into a mixture of calcic pyrophosphate and metaphosphoric acid:

$$\underset{\text{Tetrahydric calcic orthophosphate.}}{2\mathbf{P}_2\mathrm{O}_2\mathrm{Ho}_4\mathrm{Cao}''} = \underset{\text{Calcic pyrophosphate.}}{\mathbf{P}_2\mathrm{O}_3\mathrm{Cao}''_2} + \underset{\text{Metaphosphoric acid.}}{2\mathbf{P}\mathrm{O}_2\mathrm{Ho}} + \underset{\text{Water.}}{3\mathbf{O}\mathrm{H}_2},$$

but when the mixture is heated to a higher temperature, pure calcic metaphosphate remains:

$$\underset{\text{Calcic pyrophosphate.}}{P_2O_3Cao''_2} + \underset{\text{Metaphosphoric acid.}}{2PO_2Ho} = \underset{\text{Calcic metaphosphate.}}{2P_2O_4Cao''} + \underset{\text{Water.}}{OH_2}.$$

The so-called *superphosphate of lime* is a mixture of the preceding salt with calcic sulphate, and is obtained by acting upon bone-ash or a native calcic phosphate with two-thirds of its weight of sulphuric acid. It is employed as a manure, and also in the manufacture of phosphorus.

Calcic hypophosphite, $\begin{matrix}PHHo \\ PHHo\end{matrix}Cao''$, is prepared by boiling phosphorus with milk of lime:

$$\underset{\text{Calcic hydrate.}}{3CaHo_2} + 2P_4 + \underset{\text{Water.}}{6OH_2} = \underset{\text{Calcic hypophosphite.}}{3\begin{matrix}PHHo \\ PHHo\end{matrix}Cao''} + \underset{\text{Phosphoretted hydrogen.}}{2PH_3}.$$

On evaporating the solution the salt is obtained in monoclinic prisms. When heated it evolves phosphoretted hydrogen and water, leaving calcic pyrophosphate:

$$\underset{\text{Calcic hypophosphite.}}{2\begin{matrix}PHHo \\ PHHo\end{matrix}Cao''} = \underset{\text{Phosphoretted hydroden.}}{2PH_3} + \underset{\text{Calcic pyrophosphate.}}{P_2O_3Cao''_2} + \underset{\text{Water.}}{OH_2}.$$

Calcic hypophosphite is used in medicine.

Silicates of Calcium.—The following silicates of calcium occur in nature:

Wollastonite.	*Calcic silicate,*	$SiOCao''$.
Okenite.	*Tetrahydric calcic disilicate,* . . .	Si_2OHo_4Cao''.
Gurolite.	*Tetrahydric dicalcic trisilicate,* . .	$Si_3O_2Ho_4Cao''_2$.
Xonaltite.	*Dihydric tetracalcic tetrasilicate,* . .	$Si_4O_3Ho_2Cao''_4$.

Most of the natural silicates are compound silicates of calcium with other metals.

Glass.

The several varieties of glass consist of amorphous mixtures of potassic or sodic silicate with calcic or plumbic silicate. *Bohemian* or *potash-glass* is a potassic and calcic silicate. It is less fusible and resists the action of acids and alkalies better than the other varieties, for which reasons it is largely used for laboratory vessels and for combustion tubing. *Crown-glass* (*soda-glass, window-glass, plate-glass*) is a sodic and calcic silicate. It has a bluish-green tinge, which may be seen on the edge of a sheet of window-glass. *Bottle-glass* is merely a crown-glass manufactured from commoner materials. Its dark-green color is due to the presence of iron, and its brown or black appearance to finely divided carbon. It also contains alumina. *Flint-glass* is a potassic and plumbic silicate. It is remarkable for its density, lustre, and refracting power. It is the most fusible variety of glass, and is most readily attacked by chemical reagents.

The silica employed in glass-making is introduced as quartz, white sand, pulverized flints, or ordinary sand, according to the quality of the

glass required. The alkalies are added as pearl-ash (potassic carbonate) and as purified soda-ash (sodic carbonate). For inferior varieties of soda-glass, salt cake (sodic sulphate) is substituted for sodic carbonate; in this case carbon is added, which reduces the sulphate to sulphite, the sulphurous anhydride being then expelled by the silicic anhydride at the high temperature at which the glass is prepared. The calcium is added in the form of marble, limestone, or chalk. In Bohemia, wollastonite, a native calcic silicate, is employed. In the case of flint-glass, the lead is added as red-lead, white-lead, or litharge, the first of these being employed for the finer sorts.

The iron which is invariably present, even in the purest materials, would, if uncorrected, impart to the glass a green tinge, due to the formation of ferrous silicate. In order to obtain a colorless glass, an oxidizing agent is added to the mixture to convert the ferrous into a ferric salt, the latter having only a faint yellow tinge, which, when the iron is present in small quantity, is not perceptible. The oxidizing agents most frequently employed in the case of the various sorts of calcium-glass, are manganic peroxide, arsenious anhydride, and potassic or sodic nitrate; whilst, in the case of flint-glass, red-lead is used. The manganic dioxide decolorizes not only by its oxidizing action, but also by its property of producing a violet tint, complementary to the green of the ferrous silicate, the two colors thus neutralizing each other.

The materials are mixed with a certain quantity of broken glass or "cullet," and are then *fritted*, or heated to a temperature at which they begin to agglomerate. In this process of fritting, moisture and gases, such as carbonic anhydride, are expelled, and the frothing in the subsequent fusion is thus greatly diminished. The mass is then fused in pots made of a very refractory fire-clay, the fusion being continued until all the bubbles of gas have escaped, and the contents of the pot form a homogeneous liquid. The temperature is then allowed to fall until the glass becomes sufficiently viscid to permit of its being worked—either by the glass-blower, or by rolling it into plates, as in the case of plate-glass, or by pressing into moulds.

Glass which has been suddenly cooled after fusion possesses the singular combination of properties of resistance to fracture on the one hand, and on the other, extraordinary brittleness as soon as incipient fracture has, by scratching or otherwise, been induced. These properties are exhibited in a high degree by the so-called *Rupert's drops*, which are prepared by allowing melted glass to fall in drops into cold water. The glass solidifies in the form of elongated, pear-shaped drops, rounded at one end and produced to a thin tail at the other. The thick portion of these drops may be subjected to considerable violence—by pressure or by hammering—without breaking; but if the end of the thin tail be nipped off, the whole drop disintegrates with a slight explosion, and is converted into a fine powder.

The tenacity of glass thus treated is probably due to the wholly amorphous condition of the mass—the glass being cooled before the molecules have time to arrange themselves in the manner necessary to the production of a crystalline structure. Ordinary annealed glass (see below) is for the most part amorphous, but that it is also to some ex-

tent crystalline may be shown by etching the surface with hydrofluoric acid, when the crystalline structure becomes visible under the microscope. It will also be shown further on that glass may be made to acquire a highly crystalline structure by protracted heating to its softening point, a process the reverse of the above. The effect of a crystalline structure in diminishing tenacity depends upon the disturbance of the homogeneity of the mass which the growth of crystals within it necessitates, and, further, upon the unequal tenacity of most crystals in various crystallographical directions, a property which is manifested in the production of cleavage surfaces (see Crystallography, p. 131).

On the other hand, the parts of a mass of glass thus suddenly cooled, are in the state of tension or strain. Owing to the low conducting power of glass, the outer portions cool and solidify first, and in this way the inner portions, which cool later, are prevented from contracting to the extent which they otherwise would. The moment this state of unstable equilibrium is disturbed—as in the above experiment, by nipping off the tail of the drop—the whole system breaks down, and the potential energy of this tension expends itself in the disintegration of the mass.

The same phenomenon is exhibited, although in a lesser degree, in the case of articles of glass which have been cooled by exposure to air. Such articles are apt to crack when scratched or when exposed to sudden change of temperature. A bottle of thick unannealed glass may be broken to fragments by dropping into it a small sharp fragment of flint.

In order to prevent fracture from this cause, all articles of glass are subjected to a process of very slow cooling, termed *annealing*, in a suitable furnace. In this way the cooling and solidification occur homogeneously throughout the mass, the molecules can arrange themselves in the positions which they would naturally assume, and the state of strain cannot arise.

A peculiar process, intended to replace that of annealing, and at the same time to impart to the glass new and valuable properties of durability, has been introduced within the last few years by De la Bastie. The glass, heated almost to redness, is dipped into oil or paraffin, previously heated to 300° C. (572° F.), and is then allowed to cool slowly. Glass which has been subjected to this treatment, and which is known as *toughened glass*, is much less fragile than ordinary annealed glass: it resists sudden changes of temperature better, and is not so readily broken by rough usage. When broken, however, by a hard blow, it splits up into innumerable fragments. In like manner, a sheet of toughened glass cannot be cut with a diamond, as the whole instantaneously disintegrates. The glass is, therefore, to some extent at all events, in a state of internal strain similar to that of the Rupert's drops. Indeed, cases have occurred in which articles of toughened glass have, suddenly and without apparent cause, exploded with some violence.

The following table contains the results of the analysis of various kinds of glass:

Composition of various kinds of Glass.

	Bohemian glass.		Crown glass.		Bottle-glass.		Flint-glass.	
	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
SiO_2, . . .	71.7	69.2	62.8	69.2	60.0	59.0	51.9	42.5
OK_2, . . .	12.7	15.8	22.1	8.0	....	1.7	13.8	11.7
ONa_2, . . .	2.5	3.0	....	3.0	3.1	10.0	....	....
CaO, . . .	10.3	7.6	12.5	13.0	22.3	19.9	....	0.5
Al_2O_3, . . .	0.4	1.2	}	{ 3.6	8.0	1.2	....	1.8
MgO, . . .	....	2.0	} 2.6	{ 0.6	....	0.5	....	....
Fe_2O_3, . . .	0.3	0.5	}	{ 1.6	4.0	7.0	....	....
MnO, . . .	0.2	....	....	....	1.2	....	....	....
PbO, . . .	....	....	....	....	....	....	33.3	43.5
	98.1	99.3	100.0	99.0	98.6	99.3	99.0	100.0

a, Hard Bohemian glass. *b*, Softer Bohemian glass. *c*, Bohemian crown-glass. *d*, German crown-glass. *e*, French bottle-glass. *f*, English bottle-glass. *g*, English flint-glass. *h*, Guinaud's glass for optical purposes.

Certain kinds of glass, when exposed for some time to a temperature at which they soften, acquire a crystalline structure, and become opaque. This process of change, known as *devitrification*, occurs most readily in lime-glass which contains an excess of silica. Flint-glass does not devitrify. When glass is imbedded in sand or gypsum to prevent change of form, and heated strongly for several hours, it is converted into a white opaque mass, known as *Réaumur's porcelain*. Glass which readily devitrifies cannot be worked before the blowpipe.

Colored glasses are obtained by the addition of various oxides to the glass. The coloring oxides mostly employed are the following:

Red, cuprous oxide, also purple of Cassius. Violet, manganic dioxide. Blue, cobaltous oxide. Green, cupric oxide, chromic oxide, ferrous oxide, the latter producing a dull bottle-green. Yellow, antimonic oxide. Yellow, with a greenish fluorescence: uranic oxide.

COMPOUNDS OF CALCIUM WITH SULPHUR.

Calcic sulphide, CaS''.—Prepared like the barium compound (p. 467). White mass, which in moist air gradually evolves sulphuretted hydrogen. Luminous in the dark after exposure to light (see p. 467).

Calcic disulphide, $Ca\left.\begin{matrix}S''\\S''\end{matrix}\right\}, 3OH_2$, is deposited in yellow crystals from the solution obtained by boiling milk of lime with sulphur and filtering hot.

COMPOUND OF CALCIUM WITH PHOSPHORUS.

Calcic phosphide, $'P''_2Ca_2$(?).—This compound has not been prepared pure. It is formed by the direct combination of metallic calcium and phosphorus, when the two substances are heated together under petroleum. It may be obtained mixed with calcic pyrophosphate by passing the vapor of phosphorus over lime heated to redness:

$$\underset{\text{Calcic oxide.}}{14CaO} + 14P = \underset{\text{Calcic phosphide.}}{5'P''_2Ca_2} + \underset{\text{Calcic pyrophosphate.}}{2P_2O_3Cao''_2}.$$

The mixture thus obtained, which forms a reddish-brown mass, is employed in the preparation of liquid phosphoretted hydrogen (p. 343). It also contains *tricalcic diphosphide*, P_2Ca_3.

General Pfoperties and Reactions of the Compounds of Calcium.—The calcium salts, as a rule, closely resemble in their properties those of barium and strontium. Those formed with colorless acids are colorless. Calcic nitrate and calcic chloride are both soluble in absolute alcohol. From solutions of calcium salts *alkaline carbonates* precipitate calcic carbonate. The sulphate of calcium is more soluble than that of strontium; in dilute solutions of calcium salts *sulphuric acid* and soluble *sulphates* produce a precipitate only on addition of alcohol. *Ammonic oxalate* precipitates white calcic oxalate, soluble in hydrochloric and in nitric acid, insoluble in acetic acid. Calcium compounds color the non-luminous flame yellowish-red. The flame spectrum is complex; the two most characteristic lines are $Ca\alpha$ in the orange, and $Ca\beta$ in the green.

On Potable Water and on the Impurities occurring in Natural Waters.

In describing the properties of water (p. 173), it was mentioned that natural waters always contain impurities; and as some of the most important of these are compounds of two of the metals belonging to the section under consideration, it will be convenient to return here to the subject in order to complete the chemical history of water.

Pure water never occurs in nature; as soon as it quits the vaporous condition, and assumes the form of clouds and rain, it becomes more or less contaminated by atmospheric impurities. When it reaches the earth, it flows over surfaces, or percolates through strata, more or less soluble, and thus acquires further impurities in addition to, or sometimes in the place of, those which it had previously contracted from the atmosphere. It thus becomes, in some cases more, in others less, suitable for domestic use. The nature of the changes which water suffers from such influences must obviously depend, to a great extent, upon the character of the geological formations over or through which it passes. If the formation be hard and insoluble, then little saline or other matter is taken up. Thus the River Loka, in Sweden, contains only 0.07 part of solid matter in 100,000 parts of water. Loch Katrine contains 3.2 parts per 100,000, Ullswater Lake 3.9 parts, and the Dee at Aberdeen 5.7 parts per 100,000 parts of water. As a rule, however, water meets with more soluble matter than this, and the proportion generally varies from 7 to 50 parts in 100,000 parts of water. Thus the Thames and Lea contain about 30 parts, and the water of deep wells sunk into the chalk about 40 parts, per 100,000.

An excessive amount of these foreign matters renders the water unpalatable, and constitutes it a *mineral* or *abnormal water*. Such accumulations of soluble saline matter take place in the ocean, which contains from 3140 to 4000 parts per 100,000, and in lakes without outlet. Thus the Dead Sea, which is 1312 feet below the level of the Mediterranean, and is fed by the Jordan and six other streams (containing on the average 104 parts of soluble solid matter per 100,000)

contains 22,857 parts of solid matter per 100,000. And the Elton lake in Russia contains 27,143 parts per 100,000, although upwards of 200,000 tons of salt are annually extracted from it.

We propose here, however, to confine attention chiefly to drinking or potable water—a subject which is, year by year, acquiring an increased sanitary importance.

Numerous researches, made by both physiologists and chemists, have led investigators to the conclusion that several, at least, of those diseases, which are propagated in the manner of epidemics, diffuse themselves by living germs or spores, which, finding a suitable *nidus* in the bodies of animals, there multiply and produce that specific disturbance of the normal vital functions which characterizes a disease of the zymotic class. It is indeed in consequence of the extensive prevalence of this view respecting the mode of propagation of such diseases that the term zymotic (from *ζυμόω*, I ferment) has come to be almost universally employed to designate them.

Long continued observations and carefully compiled statistical records have conclusively demonstrated that drinking-water is the chief medium through which zymotic diseases, especially cholera and typhoid fever, are propagated. In these latter diseases the infectious or zymotic matter is contained in the discharges from the intestinal canal of the patient. Many of our arrangements for disposing of these secretions have the effect of diffusing them through water, and the drinking of such polluted water not unfrequently conveys the infection to whole communities. Shortly stated, it is absolutely necessary for the propagation of cholera and typhoid fever, that the excrements of persons suffering from these diseases should be swallowed by other persons. That such an unspeakably disgusting mode of infection is not only possible, but imminent over a very large proportion of the inhabitants of Great Britain, is conclusively proved by the numerous analyses of the water used by them for drinking. So far from the horrible practice just indicated being exceptional, it is the rule. It is a widely spread custom, both in towns and villages, to drink either the water of rivers into which the excrements of man are discharged, or the water from shallow wells which are largely fed by soakage from middens, sewers, or cesspools. Thus many millions of the population are daily exposed to the risk of infection from typhoidal discharges, and periodically to that from cholera dejections.

It would obviously be of the very highest importance to mankind, if the presence of cholera or typhoid poison in water could be demonstrated by chemical or microscopical analysis. This is, however, at present impossible. It is only by their action on human beings that their presence can be proved. But, chemical analysis can show us the presence, in water, of excremental matter, or of the characteristic products of its decomposition, although it cannot distinguish between normal and infected excrement.

From this point of view, therefore, the analyical examination of water assumes an importance second to no other application of chemistry. It would be out of place, however, in this work to describe the mode of performing these analyical operations, and we shall therefore

confine ourselves to an enumeration of the data obtained in water analysis and to the interpretation of these data.

Water Analysis.—The exhaustive chemical examination of a sample of water is one of the most tedious and troublesome operations known to chemists. It requires weeks, sometimes even months, for its completion. This arises partly from the great multiplicity of separate substances which may be present in the water, both in solution and in suspension, partly from the very minute proportion in which these substances sometimes exist, and partly on account of the difficulties attending their exact determination, when they are diffused through vast volumes of water. Such an exhaustive examination includes:

1. The extraction and separate volumetric measurement of the dissolved gases.
2. The separate determination of the weight of each constituent of the saline matters in solution.
3. The determination of the two chief elements of the organic matters in solution.
4. The separation of the suspended matters, if any, and the determination of their total weight when dry.
5. The separation and determination of each mineral constituent of the suspended matters.
6. The separation and determination, as far as possible, of each organic constituent of the suspended matters.

Fortunately, many of the more tedious and laborious of these operations may be omitted, if the object of the analysis be only to ascertain the suitability or otherwise of the water for domestic or manufacturing purposes. Thus, the extraction and volumetric measurement of the gases may be safely dispensed with; since, in the present state of our knowledge, the gaseous constituents of water throw but little light upon its character. The existence of dissolved atmospheric gases in water doubtless adds to its platability; recently boiled water, for instance, has a notoriously flat and vapid taste, but the solution of these gases by water is so rapid as almost to preclude the possibility of lack of aëration in natural waters. This is seen from the following comparison of the proportional volumes of atmospheric gases expelled on boiling 100 cubic centimetres of rain-water, Welsh and Cumberland upland surface water, Loch Katrine water as delivered in Glasgow, Thames water as delivered in London, and water drawn from deep wells in the chalk, respectively:

Volume and Composition of the Gases dissolved in 100 *Cubic Centimetres of Various Waters.*

	Rain water.	Cumberland mountain water.	Loch Katrine water.	Thames water.	Deep chalk well water.
Nitrogen, ...	1.308 c.c.	1.424 c.c.	1.731 c.c.	1.325 c.c.	1.944 c.c.
Oxygen, ...	0.637 "	0.726 "	0.704 "	0.588 "	0.028 "
Carbonic anhydride, .	0.128 "	0.281 "	0.113 "	4.021 "	5.520 "
	2.073 "	2.431 "	2.548 "	5.934 "	7.492 "

A comparison of the numbers in the foregoing table shows that the total volume of dissolved atmospheric gases differs but little, even in waters from the most widely different sources. It was at one time supposed that the proportion of oxygen in these gases was an important item in the history of the water, and a deficiency of this gas was believed to indicate the presence of putrescent organic matters; but the subsequent discovery that deep well waters (in which putrescent organic matter is certainly not present) contained little or no dissolved oxygen, deprived this analytical fact of much of its importance.

The large proportion of carbonic anhydride which is present in Thames water and in deep chalk well water scarcely adds to the effective aëration of these waters, because nearly the whole of this carbonic anhydride is in chemical combination with lime, and not in the condition of dissolved gas.

The separate determination of the weight of each constituent of the saline matters in solution is also rarely required. These constituents have, with very few exceptions, no appreciable influence upon the wholesomeness of the water; hence, in the great majority of cases, it is not necessary to determine the weight of each. Certain of them, however—ammonia, nitrates, nitrites, and chlorides—are very useful in tracing the previous history of the water, and the separate determination of these must, therefore, on no account be omitted. Moreover, if the presence of lead, arsenic, or barium be suspected, these poisonous metals must be carefully sought for, and, if found, their respective quantities determined. The degree of hardness ought also to be ascertained in all cases.

The separation and determination of each mineral constituent of the suspended matters may be dispensed with, unless poisonous substances occur amongst them.

The separate determination of each organic constituent of the suspended matter is of comparatively little use in the present state of our knowledge, because it is impossible to distinguish, amongst the suspended matters in water, those which are injurious from those which are harmless. The really injurious organic suspended matters are probably not merely organic but organized matters, entozoic ova, or zymotic germs, capable of reproduction in the human body with the simultaneous development of disease. Investigations of this class belong rather to microscopical than to chemical analysis, but even microscopic research is not yet competent to reveal any facts of direct importance in connection with such organized suspended matters.

The microscope has rarely if ever discovered, even in the most polluted drinking water, any germ or organism which is known to be deleterious to human health; but by showing the presence of living organisms in water, it proves, either that the water has not been so efficiently filtered as to remove these organisms, or that it has subsequently become polluted by them; and thus it is indirectly demonstrated that the water has not been treated, preserved, or stored under such conditions as would preclude the access of deleterious germs or organisms. A microscopic examination of the suspended matters in potable waters thus becomes indirectly of considerable importance.

The analytical determinations, deemed sufficiently important to warrant the expenditure upon them of the necessary time and labor, are the following; those which are of primary importance being printed in bold type:

In Solution.

1. Total solid matters.
2. **Organic carbon, or carbon contained in the organic matter actually present.**
3. **Organic nitrogen, or nitrogen contained in the organic matter actually present.**
4. Ammonia.
5. Nitrogen as nitrates and nitrites.
6. Total combined nitrogen.
7. **Estimation of the previous sewage or animal contamination.**
8. Chlorine.
9. Temporary, permanent, and total hardness.

In Suspension.

10. Mineral matters in suspension.
11. **Organic matters in suspension.**

We have now to explain the object and significance of each of these determinations.

1. *Total Solid Matters in Solution, or Total Solid Impurities.*—When water is evaporated to dryness, there is left behind a solid residue containing the mineral and organic matters with which the water had become contaminated since its condensation from the atmosphere. Leaving out of consideration the quality of the ingredients contained in potable waters, the proportion of solid residue left on evaporation affords an approximate, though rough, indication of the comparative purity of such waters. On the one hand it may be safely concluded, that waters leaving very large residues on evaporation are unfit for domestic use, whilst on the other, those containing very small residues are, on this account alone, well adapted for such purposes, and but very rarely contain amongst their constituents any which are seriously objectionable. Not only do waters leaving small residues on evaporation generally possess a superiority for domestic purposes, but they are also much more valuable than less pure waters for a large number of manufacturing purposes. Thus, for the feeding of steam boilers, their use precludes the formation of incrustations, which not only seriously interfere with the transmission of heat from the fuel to the water, but are probably a frequent cause of disastrous explosions.

2. **Organic Carbon.**—From a sanitary point of view, the most important constituent of the total solids is organic matter, and various processes have from time to time been devised for the quantitative determination of this matter or of some of its constituents. The problem is surrounded with unusual difficulties, and hitherto no method, worthy of any degree of confidence, has been discovered by which the weight of organic matter dissolved in water can be even approximately deter-

mined. Even of several analytical processes which do not pretend to the estimation of the total weight, and aim at the quantitative determination of only some of the elements of the organic matter, there is only one which yields trustworthy results. This process is both troublesome and tedious, and requires considerable manipulative skill; but it is the only method which throws any light whatever upon the actual pollution of water by organic matter. It consists in transforming by combustion in close vessels the carbon and nitrogen of the organic matter into carbonic anhydride and free nitrogen, and then measuring the respective volumes of these gases. By a simple calculation, the weights of carbon and nitrogen contained in the original organic matter present in the water can be arrived at, from these volumetric determinations, with great precision. The weight of organic carbon, or carbon contained in the organic matter found in different samples of water, indicates the amount of organic matter with which the water is contaminated, but it does not indicate the source, animal or vegetable, whence that organic matter was derived. *Cœteris paribus*, the smaller the proportion of organic carbon, the better the quality of the water. Even if the source of the organic matter be altogether vegetal, experience has shown that a proportion of organic carbon larger than 0.2 part in 100,000 parts of water is undesirable, because it renders the water slightly bitter and unpalatable. A larger proportion of organic carbon, if it be contained in animal matter, does not interfere with the palatability of the water, but it exposes the consumer to the risk of infection, and potable water which contains organic matter, even only partially derived from animal sources, should not yield much more than 0.1 part of organic carbon from 100,000 parts of water.

3. **Organic Nitrogen.**—The character of the organic matter contained in potable water, that is to say, its animal or vegetable origin, may in most cases be judged of by the relative proportions in which the two elements, carbon and nitrogen, occur in the organic matters. Hence the necessity for determining the amount of organic nitrogen in waters used for domestic purposes. This determination, taken in connection with that of organic carbon, frequently affords information of great value as to whether the organic matter is of animal or vegetable origin; and this information acquires additional importance and trustworthiness when it is subsequently tested by a chemical investigation of the previous history of the water as revealed by the proportions of the chief products derived from sewage and animal matters, viz., ammonia, nitrates, nitrites, and chlorine. The smaller the absolute quantity of organic nitrogen, and the less the proportionate amount as compared with organic carbon, the better is the quality of the water as regards present or actual pollution, and the less likely is the water to contain any organic matters of animal origin. In connection with this part of the analytical investigation, however, it must be borne in mind that vegetable organic matter is far from being destitute of nitrogen. Peat, for instance, which is a form of vegetable matter least likely to contain nitrogen, yields to water organic substances in solution containing much nitrogen. Doubtless, different samples of peat vary in the nitrogenous character of the soluble vegetable matter which they contain; but, on

the average, the proportion of nitrogen to carbon may be taken to be $N : C = 1 : 12$, and it is found that such peaty matters dissolved in water may, after prolonged exposure to oxidizing influences, lose carbon so much more rapidly than nitrogen, as materially to increase the proportion of the latter element to the former.

The following table shows the proportion of nitrogen to carbon in waters containing organic matter of peaty origin :

	Proportion of carbon to 1 part of nitrogen.
Unoxidized peaty matter contained in upland surface water, ...	11.92
Peaty matter contained in upland surface water after exposure to atmospheric oxidation in natural lakes or artificial reservoirs, ...	5.92
Peaty matter contained in spring water, ...	3.21

Thus the proportion of carbon to nitrogen in the peaty organic matter of water decreases rapidly as oxidation progresses. After storage for weeks or months in lakes it is reduced to one-half its original amount; but after the water containing the peaty matter has been subjected to the powerful oxidizing influences which accompany filtration through porous strata, it reappears as spring water with a greatly augmented proportion of organic nitrogen, although the absolute quantity has greatly diminished. In other words, large quantities of both carbon and nitrogen have been oxidized and converted into mineral matter, but the carbon has undergone this transformation more rapidly than the nitrogen.

This concentration of nitrogen during oxidation assimilates oxidized vegetable to unoxidized animal organic matter in chemical composition, so far, at least, as the proportion between the chief elements, nitrogen and carbon, is concerned. There is still, however, a considerable difference in this respect between these two kinds of organic matter; but even this disappears when the water containing animal organic matter is subjected to oxidizing influences; for whilst vegetable organic matter suffers a concentration of nitrogen during oxidation, animal organic matter exhibits, as a rule, a concentration of carbon, and a diminution in the proportion of nitrogen under the same influence.

Thus the proportions of nitrogen to carbon in soluble vegetable and animal organic matters vary in opposite directions during oxidation ; a fact which renders more difficult the decision as to whether the organic matter present in any given sample of water is of animal or vegetable origin. This difficulty can, however, be greatly diminished or entirely overcome by an appeal to the previous history of the water as revealed partly by a knowledge of its source, and of the kind of contamination to which it has been exposed, and partly through the information afforded by chemical analysis. In the first place, if the water is known by an inspection of its source to have been polluted by animal matters, and to have been subjected, after such pollution, only to the slight oxidation effected in rivers or streams, a portion at least of the organic matter which it contains must have been derived from animal matter. For

there is no river in Great Britain long enough to completely oxidize or destroy the soluble animal organic matter present in polluted water. In the second place, if the water is found, on analysis, to contain considerable quantities of one or more of the mineral compounds—ammonia, nitrates, and nitrites—into which animal organic matter is resolved during its decomposition or oxidation, the inference may be drawn that the soluble organic matter of such water is derived from animal sources. But this inference must only be provisional; it must stand or fall by an investigation into the source of the water; for although the presence of the products of the decomposition of animal matter indubitably convicts the water of previous pollution, yet it is obviously possible, from the facts and considerations which have just been adduced, that the whole of the original organic matter may have been oxidized and converted into innocuous mineral compounds during the prolonged filtration of the water through a great thickness of porous strata, and that the water so purified may afterwards have become contaminated with vegetable matter only. In other words, water polluted by animal matters may become pure spring water, retaining only the innocuous evidence of its former pollution, and may then become polluted by the soluble matter of peat. Such water would be suspicious owing to the evidence of its previous pollution, which it still bears about with it, and it could only be cleared from this suspicion on proof of efficient purification after its pollution by animal matter. To render the water safe for domestic use the animal pollution must have occurred *before* it became spring water.

It is upon this part of the investigation of potable water that the next four determinations have a very important bearing.

4. *Ammonia.*—This mineral nitrogenous compound is rarely absent from potable waters, which derive it, sometimes from the atmosphere, but more usually from decomposing animal matters. Rain water falling in London sometimes contains as much as 0.21 part of ammonia in 100,000 parts of water, but this is exceptional, and the proportion rarely exceeds one-third of that amount. The average quantity present in 71 samples of rain water collected at Rothamsted, near St. Albans, was 0.049 part in 100,000 parts of water. In river water the proportion rarely exceeds 0.01 part, in unpolluted well water it is usually less, whilst in spring water it is either absent altogether or present in only very minute proportion. On the other hand, it often abounds in the water of much polluted shallow wells. The proportion of ammonia in the London shallow well waters sometimes rises as high as 2.75 parts in 100,000 parts of water. In contact with animal matter and under the operation of oxidizing influences, ammonia is very rapidly converted into nitrites and nitrates, and its presence therefore in considerable proportion in shallow well waters indicates their very recent contamination with animal matters. Its occurrence in water from deep wells, however, does not permit of the same inference being drawn, because we find that in such water the decomposition of nitrates not unfrequently gives rise to ammonia. This is particularly the case in very deep wells, and in those which are sunk into the Chalk beneath the London Clay. The ammonia which occurs under such circumstances is obviously still more

remote from the animal matter whence it originated, than the nitrates from which it was immediately derived, and which were themselves generated by the oxidation of animal matter.

The chief significance attaching to the determination of ammonia in potable water lies in the circumstance that this compound is derived almost exclusively from the decomposition of animal matter. It is obvious, however, from the consideration just mentioned, that all inferences to be drawn from its presence must be controlled by a study of the physical and chemical history of the water.

5. *Nitrogen as Nitrates and Nitrites.*—In the presence of oxygen, the nitrogen of animal matters is transformed, in great part, into nitric acid and nitrous acid; and these, by combining with the basic substances always present in polluted water, are in their turn transformed into nitrates and nitrites. This transformation takes place most rapidly and completely when the polluted water soaks through aërated soil. Thus 97 per cent. of the combined nitrogen of London sewage is converted into nitrates during its slow percolation through a stratum of gravelly soil only 5 feet thick.

Whilst the oxidation of animal matters in solution in water yields abundance of nitrates and nitrites, vegetable matters furnish under like circumstances none, or mere traces, of these compounds. Upland waters, which have been in contact only with mineral matters or with the vegetable matter of uncultivated soil, contain, if any, mere traces of nitrogen in the form of nitrates and nitrites; but as soon as the water comes into contact with cultivated land, or is polluted by the drainage from farmyards or human habitations, nitrates in abundance make their appearance. The presence of these salts in sufficient quantity is, therefore, trustworthy evidence of the previous pollution of the water with animal matters. It must be borne in mind, however, that nitric and nitrous acids are present, though in but minute quantity, in the atmosphere, and that rain washes them out of the air through which it falls. In 71 samples of rain water collected at Rothamsted the proportion of nitrogen as nitrates and nitrites varied from 0 to 0.044 part in 100,000 parts of water. Even the highest proportion, which occurred only once, is a very small one, and one that is never met with in unpolluted upland waters.

6. *Total combined Nitrogen.*—The element nitrogen may exist in water in four forms; viz.: firstly as a constituent of organic matter, secondly as a constituent of ammonia, thirdly as a compound of nitrates and nitrites, and fourthly as a constituent of dissolved atmospheric air. In the last case, the nitrogen is in the free or elementary condition; and as it neither pollutes the water nor throws any light upon its previous pollution, it may be left out of consideration. In all the other three forms, the nitrogen is combined with other elements, constituting either polluting matter or the resultant of previously existing polluting matter. With a slight deduction for the minute amount of this element which is met with in combination in rain water, the determination of total combined nitrogen sums up, as it were, the evidence of the *past* and *present* pollution of each water by nitrogeneous organic matter of either animal or vegetable origin. The evidence is unfortunately de-

fective, especially in spring and summer, because some of the compounds containing nitrogen constitute an important part of the food of both animal and vegetable organisms. Combined nitrogen also suffers diminution whenever the organic matter in the water enters into putrefaction or undergoes oxidation in the absence of atmospheric oxygen and in the presence of nitrates and nitrites. The latter salts supply, under these circumstances, the oxygen required to transform the carbon and hydrogen of the organic matter into carbonic anhydride and water, whilst their nitrogen is converted only to a slight extent into ammonia, the rest being set free and consequently ceasing to exist as combined nitrogen. It is thus that the water of very deep wells frequently retains few or no traces of the nitrates and nitrites which it previously held in solution, whilst a comparatively small proportion of ammonia is found in their place. The artesian wells of London afford striking instances of this destruction of nitrates and consequently of combined nitrogen.

7. **Previous Sewage or Animal Contamination.**—It has been established by very numerous chemical analyses, that animal matters dissolved in water, such as those contained in sewage, the contents of privies and cesspools, or farmyard manure, undergo oxidation in lakes, rivers, and streams very slowly, but in the pores of an open soil very rapidly. When this oxidation is complete, they are resolved into mineral compounds;—their carbon is converted into carbonic anhydride, and their hydrogen into water, products which can no longer be identified in the aërated waters of a river or spring; but their nitrogen is transformed partly into ammonia, chiefly however into nitrous and nitric acids, which, combining with the bases present in nearly all water that has been in contact with the earth, form nitrates and nitrites, and frequently remain dissolved in the water for a long time;—there constituting a record of the sewage or other analogous contamination, to which it has been subjected since its last descent to the earth as rain.

It is convenient to have a concrete expression for the amount of previous animal contamination revealed by this record of the past history of water. Such an expression is obtained by taking as a standard of comparison the amount of total combined nitrogen contained in solution in 100,000 parts of average London sewage. Although a considerable proportion of this nitrogen is found at the sewer outfall in the condition of ammonia, it is well known that in the perfectly fresh sewage the nitrogen of this ammonia was present as a constituent of animal organic matter. The earlier analyses of London sewage made by Hofmann and Witt, give the number 8.363 as the amount of total combined nitrogen contained in 100,000 parts of average London sewage. More recent analyses show that 100,000 parts of average London sewage now contain only 7.06 parts of total combined nitrogen. This difference is doubtless owing to the more abundant supply of water to the metropolis at the later period. For simplicity, however, a round number (10) is assumed as the amount of total combined nitrogen in solution in 100,000 parts of average London sewage.

In estimating, in terms of this standard, the previous animal contamination of water, from the proportion of nitrogen, in the form of ammonia and of nitrates and nitrites, which it holds in solution, it is

necessary to bear in mind that rain water itself contains these substances, although in minute quantities. The average composition of samples of rain water collected at Rothamsted gives the amount of nitrogen in these forms as 0.032 in 100,000 parts of water.

After this number (0.032) has been substracted from the amount of nitrogen, in the forms of nitrates, nitrites, and ammonia, found in 100,000 parts of a potable water, the remainder, if any, represents the nitrogen derived from oxidized animal matters with which the water has been in contact. Thus a sample of water which contains, in the forms of nitrates, nitrites, and ammonia, 0.326 part of nitrogen in 100,000 parts, has obtained $0.326 - 0.032 = 0.294$ part of that nitrogen from animal matters. Now this last amount of combined nitrogen is assumed to be contained in 2940 parts of average London sewage, and hence such a sample is said to exhibit 2940 parts of previous sewage or animal contamination in 100,000 parts; or in other words, 100,000 lbs. of the water contain the mineral residue of an amount of animal organic matter equal to that found in 2940 lbs. of average London sewage.

It must not be forgotten, however, that the absence of nitrogen in these forms is not absolutely conclusive evidence of immunity from this pollution. There are several agencies at work by which this testimony, as to the amount of animal matter previously in the water, may be weakened or altogether destroyed. Thus we look in vain for the full evidence of previous animal pollution in the effluent water from fields irrigated with sewage; because the growing plants have removed a considerable proportion of ammonia, nitrates, and nitrites, from the liquid as it flows amongst their rootlets. In like manner the aquatic vegetation of rivers, lakes, and reservoirs, slowly removes these compounds from the water, and to that extent destroys the evidence of anterior animal contamination. Nitrates and nitrites are also rapidly destroyed when the organic matter in the water containing them enters into putrefaction, a condition which often occurs in streams or reservoirs containing much polluting organic matter. The same not unfrequently takes place in water-bearing strata far removed from the surface, although the water in this case may contain but a comparatively small amount of organic matter; the latter, however, cut off from a supply of atmospheric oxygen—as in the Chalk beneath the London Clay for instance—accomplishes its oxidation at the expense of the nitrates or nitrites, and thus destroys them. Owing to this cause, the evidence of previous animal contamination is not met with in the water of some deep wells in which it might otherwise be expected to occur.

The previous animal contamination of water, as deduced from chemical analysis, must therefore always be regarded as a minimum quantity; it does not denote the *comparative* freedom of different samples of water from anterior pollution; but whenever analysis shows this excess of nitrogen in the shape of nitrates, nitrites, and ammonia, the water stands convicted of previous contamination at least to the extent so indicated.

The importance of the history of water as regards its anterior pollution with organic matters of animal origin, does not arise from the

presence of the inorganic residues (nitrates, nitrites, and ammonia) of the original polluting matters, for these are in themselves innocuous, but from the risk lest some portion (not detectable by chemical or microscopical analysis) of the noxious constituents of the original animal matters should have escaped that decomposition, which has resolved the remainder into innocuous mineral compounds. This evidence of previous contamination implies, however, much more risk when it occurs in water from rivers and shallow wells, than when it is met with in the waters of deep wells or of deep-seated springs. In the case of river water, there is great probability that the morbific matter, sometimes present in animal excreta, will be carried rapidly down the stream, escape decomposition, and produce disease in those persons who drink the water; for the organic matter of sewage undergoes decomposition very slowly when it is present in running water. In the case of shallow well water, the decomposition and oxidation of the organic matter are also very liable to be incomplete during the rapid passage of polluted surface water into shallow wells. In the case of deep well and spring water, however, if the proportion of previous contamination do not exceed 10,000 parts in 100,000 parts of water, this risk is very inconsiderable, and may be regarded as *nil* if the direct access of water from the upper strata be rigidly excluded; because the prolonged filtration to which such water has been subjected in passing downward through so great a thickness of soil or rock, and the rapid oxidation of the organic matters contained in water, when the latter percolates through a porous and aërated soil, afford a considerable guarantee that all noxious constituents have been removed.

It has been already stated that chemical analysis cannot discover the noxious ingredient or ingredients in water polluted by infected sewage or animal excreta; and as it cannot thus distinguish between infected and non-infected sewage, the only perfectly safe course is to avoid altogether the use, for domestic purposes, of water which has been polluted with excrementitious matters.

Nevertheless, as it is very difficult in some localities to obtain water which has not been more or less polluted by excrementitious matters, it is desirable to classify such previously contaminated drinking waters into

Reasonably safe water.
Suspicious or doubtful water.
Dangerous water.

Reasonably Safe Water.—Water, although it exhibits previous sewage or animal contamination, may be regarded as reasonably safe when it is derived either from deep wells (say 100 feet deep), or from deep-seated springs; provided that all contaminated surface water has been rigidly excluded from the well or spring, and that the proportion of previous contamination does not exceed 10,000 parts in 100,000 parts of water.

Suspicious or doubtful water is, first, river or flowing water which exhibits any proportion, however small, of previous sewage or animal contamination; and, secondly, well or spring water containing from

10,000 to 20,000 parts of previous contamination in 100,000 parts of water.

Dangerous water is, first, river or flowing water which exhibits more than 20,000 parts of previous animal contamination in 100,000; secondly, river or flowing water containing less than 20,000 parts of previous contamination in 100,000 parts, but which is known, from an actual inspection of the river or stream, to receive sewage, either discharged into it directly or mingling with it as surface drainage; thirdly, as the risk attending the use of all previously contaminated water increases in direct proportion to the amount of such contamination, well or deep-seated spring water exhibiting more than 20,000 parts of previous contamination in 100,000 must be regarded as dangerous.

River or running water, containing less than 10,000 parts of previous animal contamination, should only be provisionally placed in the class of suspicious waters, pending an inspection of the banks of the river and tributaries; which inspection will obviously transfer it either to the class of reasonably safe waters, if the previous contamination be derived exclusively from spring water, or to the class of dangerous waters, if any part of the previous contamination be traced to the direct admission of sewage or excrementitious matters.

8. *Chlorine.*—The chlorine found in potable waters is always combined with other elements, and chiefly with sodium in the form of sodic chloride or common salt. A knowledge of the proportion of chlorine in water often throws important light upon the history of the water as regards its previous contamination with the liquid, as distinguished from the solid excrements of animals. Human urine contains about 500 parts of chlorine or 824 parts of common salt in 100,000 parts, whilst upland surface water free from previous or present pollution rarely contains more than 1 part of chlorine or 1.648 parts of common salt in the same weight; and it is present in but comparatively minute proportion in the solid excrements of animals. It is scarcely necessary to state that the determination becomes valueless, for the purpose of indicating previous sewage contamination, in the neighborhood of the sea and of natural deposits of salt. The normal proportion of chlorine, as common salt, existing in British waters which have never been polluted by excrementitious matters is, as just stated, about 1 part in 100,000 parts of water; but it varies considerably in different parts of the country. Thus at the Land's End with a strong wind from the S.W. even rain water contains as much as 21.8 parts of chlorine in 100,000 parts, while the Gelder Burn at Balmoral contained on March 9th, 1872, only 0.35 part in 100,000 parts. Unpolluted rivers and lakes in inland countries contain still less. Thus the Rhine at Schaffhausen contains only 0.2 part, and the lakes of Zug and Zürich 0.27 and 0.17 part respectively in 100,000 parts of water. The proportion of chlorine in rain water varies in like manner, and the variation is also here doubtless due to the varying distance from the sea at which the rain falls. Thus whilst rain water at the Land's End was found to contain 21.8 parts, the average proportion of rain falling in the centre of India was only 0.03 part.

9. *Hardness.*—Some of the mineral substances which occur in solution in potable waters communicate to the latter the quality of hardness. Hard water decomposes soap, and cannot be efficiently used for washing. The chief hardening ingredients met with in potable waters are the salts of lime and magnesia. In the decomposition of soap, these salts form curdy and insoluble compounds containing the fatty acids of the soap, and the lime and magnesia of the salts. So long as this decomposition goes on, the soap is useless as a detergent, and it is only after all the lime and magnesia salts have been decomposed at the expense of the soap, that the latter begins to exert a useful effect; as soon as this is the case, however, the slightest further addition of soap produces a lather when the water is agitated, but this lather is again destroyed by the addition of a further quantity of the hard water. Thus the addition of hard water to a solution of soap, or the converse of this operation, causes the production of the insoluble curdy matter above mentioned. These facts render intelligible the process of washing the skin with soap and hard water: The skin is first wetted with the water and then soap is applied; the latter soon decomposes all the hardening salts contained in the small quantity of water with which the skin is covered, and there is then formed a strong solution of soap which penetrates into the pores. This is the process which goes on whilst a lather is being produced in personal ablution; and now the lather, and the impurities which it has imbibed, require to be removed from the skin,—an operation which can be performed in one of two ways, viz., either by wiping the lather off with a towel, or by rinsing it away with water. In the former case, the pores of the skin are left filled with soap solution; in the latter they become clogged with the greasy, curdy matter which results from the action of the hard water upon the solution which had previously gained possession of the pores of the cuticle. As the latter process of removing the lather is the one universally adopted, the operation of washing with soap and hard water is analogous to that used by the dyer and calico printer when he fixes his pigments in calico, woollen, or silk tissues. The pores of the skin are filled with insoluble, greasy, and curdy salts of the fatty acids contained in the soap, and it is only because the insoluble pigment produced is white, or nearly so, that such a repulsive operation is tolerated. To those, however, who have been accustomed to wash in soft water, the abnormal condition of the skin thus induced is for a long time extremely unpleasant.

Of the hardening salts present in potable water, carbonate of lime is the one most universally met with; and to obtain a numerical expression for this quality of hardness, a sample containing 1 lb. of carbonate of lime or its equivalent of other hardening salts in 100,000 lbs. is said to have one degree of hardness. Each degree of hardness indicates the destruction and waste of 12 lbs. of the best hard soap by 100,000 lbs. or 10,000 gallons of the water, when used for washing.

Hard water frequently becomes softer after it has been boiled for some time. When this is the case, a portion at least of the original hardening effect is due to the acid carbonates of lime and magnesia. These salts are decomposed in boiling water into free carbonic anhydride, which escapes, and the carbonates of lime and magnesia. The

latter, being nearly insoluble in water, cease to exert more than a very slight hardening effect. As the hardness resulting from the carbonates of lime and magnesia is thus removable by boiling the water, it is designated *temporary hardness*, whilst the hardening effect which is due chiefly to the sulphates of lime and magnesia, and cannot be got rid of by boiling, is termed *permanent* hardness. The *total* hardness of a water is therefore commonly made up partly of temporary and partly of permanent hardness.

Hard water not only acts injuriously when it is used for washing; but, when it is employed for the generation of steam, it forms troublesome and dangerous incrustations in the boiler. A constant supply of hot water has become almost a necessity in every household, but great difficulties are thrown in the way of its attainment by the supply of hard water to towns, owing to the formation of thick calcareous crusts in the heating apparatus. Waters which have much temporary hardness are most objectionable in this respect, and the evil is so great where the heating is effected in a coil of pipe, as practically to prevent the use of this most convenient mode of heating water.

The hardness of rain water varies from 0° to 10°. The latter degree of hardness is, however, only attained near the seashore and in rough weather. At Rothamsted, in seventy-one samples, it never exceeded 1.7° and averaged only 0.49°. The hardness of water which has once touched the earth depends obviously upon the character of the gathering ground or water-bearing stratum over or through which it passes, and also upon the length of time during which it has been in contact with the earth. Calcareous and magnesian soils or strata cause the water passing over or through them to be hard. If the calcareous or magnesian matter contain carbonate of lime or carbonate of magnesia, a portion at least of the hardness will be temporary. If, on the other hand, gypsum (sulphate of lime) be the calcareous material, the hardness will be permanent. Unpolluted water collected from Igneous rocks, either as surface drainage or springs, is the softest. Its hardness varies from 0.4° to 5.9°, and averages 2.4°. Next to this in softness, must be ranged the unpolluted waters from Metamorphic, Cambrian, Silurian, and Devonian rocks, the Millstone Grit, London Clay, and Bagshot Beds, which range from 0.4° to 32.5°, and average 5.6°. The Lower Greensand also yields very soft water (about 4° of hardness) when the water does not previously percolate through calcareous strata, but this is so rarely the case as to prevent any reliance from being placed upon the softness of Greensand water. The hardness of unpolluted Greensand water sometimes ranges as high as 44°.

Amongst the slightly calcareous strata, the New Red Sandstone generally yields water of medium hardness; a large proportion of the hardness is, however, frequently permanent. In fifty-one samples of unpolluted New Red Sandstone water, the temporary hardness ranged from 0° to 19.8°, and averaged 7.7°; whilst the total hardness varied from 5.7° to 35.7°, and averaged 17.9°.

Of true calcareous strata, the Mountain Limestone yields water of least total hardness, whilst the permanent hardness is in general only a small proportion of the total. The analysis of nineteen samples of un-

polluted limestone water showed a total hardness varying from 9.8° to 27.9°, and averaging 15.7°. The permanent hardness ranged from 3.3° to 12.9°, and averaged 7.1°.

The Dolomite or Magnesian Limestone generally imparts to water great hardness, of which a large proportion, and sometimes nearly the whole, is permanent. This stratum occupies, however, a comparatively small area in this country, and the water is consequently but little used for domestic purposes. In five samples the total hardness varied from 14.7° to 67.3°, and averaged 41.2°; whilst the permanent hardness varied from 8.3° to 40.8°, averaging 24.8°; and the temporary hardness from 0.8° to 26.5°, averaging 16.4°.

The Lias yields water of variable, but nearly always great, hardness. The permanent hardness of water from this geological formation is also almost invariably high. In ten samples, the total hardness ranged from 10.3° to 50°, and averaged 29°; the permanent hardness varied from 1.7° to 17.4°, averaging 8.2°; and the temporary hardness from 8.6° to 35.3°, averaging 20.9°.

The Oolite and Chalk strata yield water of great, but chiefly temporary, hardness. In forty-two samples of unpolluted Oolitic water, the total hardness ranged from 4.2° to 35.2°, and averaged 22.4°; the permanent hardness varied from 3.5° to 13.5°, averaging 6.1°; whilst the temporary hardness was from 0° to 25.7°, and on the average 16.3°.

In ninety-five samples of unpolluted water from the Chalk, the total hardness ranged from 12.4° to 50°, and averaged 26.1°; the permanent hardness ranged from 2.7° to 13.8°, averaging 6.1°; whilst the temporary hardness varied from 6.8° to 38.6°, and averaged 20.2°.

The Chalk beneath the London Clay yields water which is usually much softer than that obtained from Chalk which is not covered by an impervious stratum. In fourteen samples of water from this source, the total hardness ranged from 0.9° to 48.5°, the average being 18.9°; the permanent hardness varied from 0.9° to 25.4°, but this extreme number and the extreme of total hardness occurred only in the water from a deep well at Harrow-on-the-Hill. Omitting this well, the extreme total hardness was 28.2° and the extreme permanent hardness 9.7°; whilst, omitting the Harrow sample, the temporary hardness varied from 0° to 21.2, and averaged 7.1°.

The Coal Measures yield water of very variable hardness, owing to the variety in chemical composition presented by these rocks. The surface waters are generally very soft, but those derived from springs and deep wells are not unfrequently very hard. In sixty samples, the total hardness varied from 2.3° to 75°, and averaged 14.7°; the permanent hardness ranged from 1.2° to 48.5°, and averaged 9.6°; whilst the temporary hardness varied from 0° to 28.2°.

Water obtained from any stratum permeable to the foul liquids of sewers, middens, and cess-pits is always hard, and generally exhibits a large proportion of permanent hardness. The food of man and beast contains considerable quantities of lime, nearly the whole of which, in the adult, is discharged in the liquid and solid excrements. In 258 samples of shallow well water polluted by excrementitious matters to such an extent as to exhibit evidence of 10,000 parts and upwards of

previous sewage or animal contamination, the total hardness ranged from 9.8° to 191°, and averaged 50.7°; the permanent hardness varied from 3.8° to 164.3°, and averaged 31.7°; whilst the temporary hardness ranged from 0° to 49.2°, and averaged 19°.

10. *Mineral Matters in Suspension.*—The mineral matters in suspension in potable water are almost invariably of an innocuous character, but they diminish or altogether destroy the transparency and brilliancy of the water, and impart a repulsive appearance, which often leads to the rejection of a wholesome water for a bright and sparkling though dangerous one. Slow filtration through sand is almost invariably effective for the removal of visible suspended matters, but the washings of clay soils are very difficult to render bright by sand filtration; and in all cases filtered water, if turbid previous to filtration, may always be shown, by suitable optical means, to be full of minute suspended particles, although to unassisted vision it is perfectly clear and transparent.

11. **Organic Matters in Suspension.**—The organic matters in suspension in potable water possess not only all the objectionable qualities of similar matters of mineral origin, but in addition they are sometimes actively injurious, and they always promote the development of crowds of animalcules. Their presence in drinking water is therefore much more objectionable than is the occurrence of mineral matters in suspension. Like the suspended mineral matters, the finely divided organic matters in suspension cannot be entirely removed by sand filtration.

The Sixth Report of the Rivers Pollution Commission gives the result of the chemical examination of 1272 samples of potable water collected under the most widely different conditions, and comprehending 81 samples of rain water, 372 samples of surface water, 419 samples of shallow well water, 180 samples of deep well water, and 220 samples of spring water. This extended investigation of waters which have drained from the surface of, or percolated through the most important geological formations of, Great Britain affords, the Commissioners say, a broad basis hitherto unattainable upon which to found conclusions as to the relative merits of potable waters from these various sources. The results of this research are quite conclusive as to the sources from which the best water for domestic purposes is to be obtained. They show that rain water contains the smallest proportion of total solid impurity, but by no means the smallest proportion of that most objectionable of impurities, organic matter. The rain drops concentrate within themselves the organic dust and dirt diffused through vast volumes of atmospheric air, and everywhere visible when a ray of sunlight illuminates them. Rain water, collected from the roofs of houses at a distance from towns, carefully stored and filtered, may be made into a fairly good and wholesome potable water; but when it is collected from the surface of uncultivated land, allowed to subside in lakes or reservoirs, or filtered through sand, it becomes of good quality for domestic, and still more so for manufacturing purposes. Numerous large towns, both in England and Scotland, are supplied with water of this description. Non-calcareous strata are generally selected as gathering ground, and then the water is soft and well adapted both for washing and for almost all manufacturing operations. It is nearly

always wholesome, but sometimes suffers in palatability by containing an excessive quantity of peaty matter in solution. This evil may be materially abated by the use of sand filters.

Seeing that rapid filtration through a few feet of sand can materially improve the quality of surface water, by removing some of the organic impurity which it contains in solution, we are prepared to find a much greater improvement when the water is drawn from deep wells or springs, to which it could only gain access by slow natural percolation through a great thickness of porous rock or earth. Under such circumstances, the powerful oxidizing influences of a porous and aërated soil are brought to bear upon the organic matter dissolved in the water. It is not, therefore, surprising to find that surface water should be almost, or even quite, exhaustively purified from such matter, by the natural intermittent filtration which transforms it into spring or deep well water. Mere exposure to the air, however, even if accompanied by violent agitation, is comparatively powerless for the removal of polluting organic matter from water.

Surface water, draining from cultivated land, is always more or less polluted with the organic matter of manure. Such water, of course, contributes very largely to rivers and streams which have already descended from their mountain or upland sources. Even when not contaminated by the actual admission into it of the sewage of towns and villages, it is not of suitable quality for domestic purposes, but when it is further polluted by excremental drainage, its use for drinking and cooking becomes fraught with great risk to health. Still more dangerous to health is the water drawn from shallow wells, no matter upon what geological formation they may be sunk, when they are situated, as is usually the case, near privies, drains, or cesspools. Many severe outbreaks of epidemic disease have been traced to the use of such water in villages and towns, and there is strong reason to believe that sporadic attacks of typhoid fever often occur in isolated country houses from the same cause.

In respect of wholesomeness, palatability, and general fitness for drinking and cooking, waters may be classified in the following order of excellence:

Wholesome.	1. Spring water.	Very palatable.
	2. Deep well water.	
	3. Upland surface water.	Moderately palatable.
Suspicious.	4. Stored rain water.	
	5. Surface water from cultivated land.	Palatable.
Dangerous.	6. River water to which sewage gains access.	
	7. Shallow well water.	

Preference should always be given to spring and deep well water for purely domestic purposes, over even upland surface water—not only on account of the much greater intrinsic chemical purity and palatability of these waters, but also because their physical qualities render them peculiarly valuable for domestic supply. They are almost invariably

clear, colorless, transparent, and brilliant—qualities which add greatly to their acceptability as beverages—whilst their uniformity of temperature throughout the year renders them cool and refreshing in summer and prevents them from freezing readily in winter. Such waters are of inestimable value to communities, and their conservation and utilization are worthy of the greatest efforts of those who have the public health under their charge.

The foregoing remarks have reference exclusively to the use of water for drinking and cooking—applications of paramount importance from a sanitary point of view; but a large proportion of the water supplied for domestic purposes is used for washing, whilst in many towns considerable volumes are used in manufactories. For all these latter purposes it is of the utmost importance that the water should be soft—a quality that is not always associated with wholesomeness and palatability. Classified according to softness, the waters from the various sources fall into the following order:

1. Rain water.
2. Upland surface water.
3. Surface water from cultivated land.
4. Polluted river water.
5. Spring water.
6. Deep well water.
7. Shallow well water.

The interests of the laundress and of the manufacturer are thus evidently opposed to those of the householder, inasmuch as they lead to a preference for moderately palatable or even unwholesome water over that which is very palatable and wholesome. Most of the hard waters from springs and deep wells can, however, be easily and cheaply rendered soft, and the interests of the householder and manufacturer thus made identical. In Clark's process of softening water with lime, the sanitary authorities of towns have at their disposal a method of rendering hard water from springs or deep wells available for washing and manufacturing purposes, without diminishing either its palatability or its wholesomeness.

The influence of geological formation upon the palatability and wholesomeness of water is very considerable. In the case of surface water this influence is to a great extent masked, or indeed often altogether annulled, by superficial deposits of vegetable matters, such as peat, upon the rocks; and thus, except in respect of hardness and saline constituents, unpolluted surface waters from the most widely different geological formations differ but little in the proportions of organic matter which they contain, and consequently in their palatability and wholesomeness. But when the water percolates or soaks through great thicknesses of rock, its quality, when it subsequently appears as spring or deep well water, depends greatly upon the nature of the material through which it has passed. When the formation contains much soluble saline matter, the water becomes loaded with mineral impurities, as is frequently the case when it percolates through certain of the Carboniferous

rocks, the Lias, and the Saliferous Marls. When the rock is much fissured, or permeated by caverns or passages, like the Mountain Limestone, for instance, the effluent water differs but little from surface drainage, and retains most of the organic impurities with which it was originally charged. But when the rock is uniformly porous, like the Chalk, Oolite, Greensand, or New Red Sandstone, the organic matter, at first present in the water, is gradually oxidized and transformed into innocuous mineral compounds. In effecting this most desirable transformation, and thus rendering the water sparkling, colorless, palatable, and wholesome, the following water-bearing strata are the most efficient:

1. Chalk.
2. Oolite.
3. Greensand.
4. Hastings Sand.
5. New Red and Conglomerate Sandstone.

This is seen from the following table, in which the average composition of unpolluted water from various sources is contrasted:

Average Composition of Unpolluted Potable Waters.

Results of Analysis expressed in parts per 100,000.

Description.	Dissolved Matters.								Hardness.			Number of samples analyzed.
	Total Solid Matters.	**Organic Carbon.**	**Organic Nitrogen.**	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Combined Nitrogen.	**Previous Sewage or Animal Contamination.**	Chlorine.	Temporary.	Permanent.	Total.	
RAIN WATER, ...	2.95	**0.070**	**0.015**	0.029	0.003	0.042	**42**	0.22	....	....	0.3	39
UPLAND SURFACE WATERS.												
From Non-Calcareous Strata.												
From Igneous Rocks, ...	5.15	**0.278**	**0.033**	0.001	0.002	0.035	**0**	1.13	0.1	2.0	2.1	18
From Metamorphic, Cambrian, Silurian, and Devonian Rocks	5.12	**0.293**	**0.024**	0.002	0.006	0.031	**3**	0.92	0.3	2.5	2.5	81
From Yoredale and Millstone Grits and the Coal Measures,	8.75	**0.373**	**0.037**	0.003	0.010	0.050	**6**	1.05	0.4	4.3	4.7	47
From Lower London Tertiaries and Bagshot Beds, ...	8.40	**0.379**	**0.048**	0.004	0.007	0.058	**0**	2.06	0.3	3.5	3.8	3

From Calcareous Strata.												
From Calcareous portions of Silurian and Devonian Rocks,	13.71	**0.302**	**0.026**	0.000	0.021	0.047	**77**	1.20	1.2	7.4	8.6	3
From Mountain Limestone, .	17.07	**0.370**	**0.047**	0.001	0.011	0.059	**26**	1.24	5.7	7.0	12.7	7
From Calcareous portions of the Coal Measures, ...	22.79	**0.346**	**0.037**	0.003	0.016	0.056	**33**	1.52	4.0	8.3	12.3	26
From the Lias, New Red Sandstone, Conglomerate Sandstone, and Magnesian Limestone, ...	18.80	**0.286**	**0.042**	0.002	0.010	0.054	**4**	1.49	7.6	6.5	14.1	9
From the Oolites, ...	17.46	**0.326**	**0.025**	0.004	0.042	0.070	**130**	1.55	6.6	5.8	12.4	1
DEEP WELL WATERS.												
In Devonian Rocks and Millstone Grit, ...	32.68	**0.068**	**0.012**	0.005	0.294	0.310	2,671	2.70	8.8	8.6	17.4	7
In the Coal Measures, . . .	83.10	**0.119**	**0.034**	0.044	0.207	0.278	2,243	18.05	15.1	20.6	35.7	9
In Magnesian Limestone, . .	61.14	**0.076**	**0.030**	0.000	1.426	1.456	**13,937**	4.31	16.9	26.9	43.8	3
In New Red Sandstone, . . .	30.63	**0.036**	**0.014**	0.003	0.717	0.734	6,895	2.94	7.4	10.5	17.9	28
In the Lias, ...	70.98	**0.146**	**0.027**	0.001	0.389	0.417	3,730	4.42	21.9	8.2	30.1	2
In the Oolites, ...	33.60	**0.037**	**0.010**	0.022	0.625	0.654	6,118	2.69	13.8	6.8	20.6	5
In the Hastings Sand, Greensands, and Weald Clay, . .	45.20	**0.068**	**0.014**	0.016	0.196	0.223	1,864	5.38	16.8	10.5	27.3	20
In the Chalk, ...	36.88	**0.050**	**0.017**	0.001	0.610	0.628	5,801	2.76	21.2	6.5	27.7	66
In the Chalk below London Clay, ...	78.08	**0.093**	**0.028**	0.048	0.068	0.135	797	15.02	9.7	8.7	18.4	13
In Thanet Sand and Drift, . .	53.84	**0.113**	**0.020**	0.072	0.116	0.202	1,517	6.32	14.4	7.6	22.0	4
SPRING WATERS.												
From Granite and Gneiss Rocks	5.94	**0.042**	**0.008**	0.001	0.106	0.115	846	1.69	0.4	2.6	3.0	8
From Silurian Rocks, ...	12.33	**0.051**	**0.014**	0.001	0.178	0.192	1,587	1.84	1.5	5.3	6.8	15
From Devonian Rocks and Old Red Sandstone, ...	25.06	**0.054**	**0.012**	0.001	0.764	0.777	7,339	3.85	4.8	7.2	12.0	22

Description.	Dissolved Matters.											Number of samples analyzed.
	Total Solid Matters.	Organic Carbon.	Organic Nitrogen.	Ammonia.	Nitrogen as Nitrates and Nitrites.	Total Combined Nitrogen.	Previous Sewage or Animal Contamination.	Chlorine.	Hardness.			
									Temporary.	Permanent.	Total.	
From Mountain Limestone, .	32.06	**0.087**	**0.010**	0.001	0.224	0.235	2,008	4.63	10.9	8.9	19.8	15
From Yoredale and Millstone Grits and the Coal Measures,	21.91	**0.050**	**0.014**	0.001	0.393	0.408	3,704	1.85	5.2	7.9	13.1	22
From Magnesian Limestone, .	66.52	**0.058**	**0.038**	0.002	1.686	1.726	**16,560**	3.40	24.9	34.8	59 7	1
From New Red Sandstone, . .	28.69	**0.065**	**0.017**	0.001	0.330	0.349	3,047	2.19	8.1	10.7	18 8	15
From the Lias, ...	36.41	**0.073**	**0.019**	0.001	0.467	0.487	4,406	2.48	21.3	8.8	30.1	7
From the Oolites, ...	30.33	**0.043**	**0.011**	0.001	0.402	0.414	3,730	1.55	18.2	6.2	24 4	35
From the Hastings Sand and Greensands, ...	30.05	**0.053**	**0.012**	0.000	0.326	0.338	2,941	2.98	13.6	6.6	20.2	19
From the Chalk, ...	29.84	**0.044**	**0.010**	0.001	0.382	0.392	3,511	2.45	18.1	5.5	23.6	30
From Fluvio-marine, Drift, and Gravel, ...	61.32	**0.086**	**0.019**	0.001	0.354	0.374	3,264	2.76	18.0	19.6	37.6	10

MAGNESIUM, Mg.

Atomic weight = 24.4. *Probable molecular weight* = 24.4. *Sp. gr.* 1.743. *Fuses at a red heat. Volatilizes at a red heat. Atomicity* ''. *Evidence of atomicity:*

Magnesic chloride, ...	$\mathbf{Mg}''Cl_2$.
Magnesic oxide, ...	$\mathbf{Mg}''O$.
Magnesic hydrate, ...	$\mathbf{Mg}''Ho_2$.

History.—Magnesic sulphate was described and its medicinal properties pointed out by Grew at the close of the seventeenth century. The metal was first isolated by Davy.

Occurrence.—The compounds of magnesium are widely distributed in nature. It occurs as carbonate in *magnesite*, $\mathbf{C}OMgo''$; as dihydric magnesic sulphate in *kieserite*, $\mathbf{S}OHo_2Mgo''$, and *Epsom salts*, $\mathbf{S}OHo_2Mgo'',6\mathbf{O}H_2$; as silicate in *enstatite*, $\mathbf{Si}OMgo''$, in *ophite* or noble serpentine, $\mathbf{Si}_2OMgo''_3$, in *talc*, $\mathbf{Si}_5O_6Mgo''_4$, and other minerals. In combination with other bases, as double salts, it occurs in enormous quantities as *dolomite*, a carbonate of isomorphous calcium and magnesium, $m\mathbf{C}OCao'',n\mathbf{C}OMgo''$;* as *kainite*, $\mathbf{S}O_2Ko\left({O \atop Cl}Mg\right),3\mathbf{O}H_2$; as *carnallite*, $\mathbf{Mg}Cl_2,KCl,6\mathbf{O}H_2$; and in a great number of silicates. The sulphate and chloride are also found in saline springs and in sea-water. It occurs in small quantities in the animal and vegetable kingdoms: thus, in the bones of animals and in the seeds of plants.

Preparation.—Magnesium may be obtained by the electrolysis of the fused chloride, but is more conveniently prepared by the action of sodium on the chloride. A mixture of 6 parts of fused magnesic chloride, 1 part of powdered fluorspar, 1 part of a mixture of sodic and potassic chloride in equal molecular proportions, and 1 part of sodium in small pieces, is thrown into a red-hot crucible, which is quickly closed. As soon as the reaction is over the crucible is removed from the fire and allowed to cool to below redness, after which the contents are stirred with a pipe-stem, in order to cause the globules of magnesium to unite. When quite cold, the solidified slag is broken up, and the magnesium removed. Magnesium is now manufactured on a large scale.

Properties.—Magnesium is a silver-white lustrous metal, of sp. gr. 1.743. The pure metal preserves its lustre in dry air, but becomes covered with a film of oxide when exposed to the action of moisture. At a higher temperature it may be pressed into the form of wire or ribbon, an operation which must be performed with exclusion of air. It fuses at a red heat, and may be distilled in a current of hydrogen. Magnesium wire or ribbon may be ignited at the flame of a candle, and burns with an intensely brilliant white light very rich in chemically active rays, a property which has led to its use in photography. Pure

* See p. 65.

magnesium does not decompose water even at 100° C. (212° F.). Dilute acids dissolve it with violent evolution of hydrogen. Unlike zinc it does not evolve hydrogen when heated with solutions of caustic alkalies. This is due to the fact that the magnesic hydrate, which would be formed, is not soluble in the alkali. Magnesium gives off hydrogen when heated with solutions of ammonia salts, the magnesium dissolving in the form of a double salt of magnesium and ammonium.

Uses.—Except for laboratory purposes, magnesium is employed exclusively in the production of the magnesium light. Besides its application in photography already referred to, the magnesium light has been used in signalling. The light has been seen at sea at a distance of 28 miles.

COMPOUNDS OF MAGNESIUM WITH THE HALOGENS.

MAGNESIC CHLORIDE, $MgCl_2$.—This compound occurs in sea-water and in salt deposits. It is formed when the metal, the oxide, or the carbonate, is dissolved in hydrochloric acid. On concentrating the solution, the chloride is deposited in monoclinic crystals of the formula $MgCl_2,6OH_2$, which when heated give off their water of crystallization, but at the same time are partially resolved into magnesic oxide and hydrochloric acid. In order to obtain the anhydrous salt in a state of purity, 12 parts of the commercial oxide are dissolved in hydrochloric acid; the solution is shaken with an excess of oxide, in order to precipitate alumina and iron, and, after filtering, evaporated to dryness with 27 parts of ammonic chloride. The resulting magnesic ammonic chloride is carefully heated to expel the water of crystallization, and is afterwards ignited in a platinum crucible, until fumes of ammonic chloride cease to be given off, and the whole has fused to a clear liquid. The anhydrous chloride solidifies on cooling to a colorless laminated crystalline mass with a lustrous fracture. It deliquesces when exposed to moist air, dissolves in water with evolution of heat, and is also readily soluble in alcohol. It volatilizes at a bright red heat. Magnesic chloride is employed in dressing cotton goods.—Magnesic chloride combines with magnesic oxide to form oxychlorides of varying composition. If strongly ignited magnesia be made into a paste with a concentrated solution of magnesic chloride, the mixture solidifies in the course of a few hours to a solid mass, sufficiently hard to be polished.

Magnesic potassic chloride, $MgCl_2,KCl,6OH_2$, occurs native as *carnallite* in large deposits at Stassfurt, and is frequently deposited from the last mother-liquors of sea-water and brine-springs. It forms colorless rhombic prisms, which deliquesce on exposure to the air. On heating, the water of crystallization is expelled without decomposition of the salt, and the anhydrous salt fuses at a red heat. Anhydrous carnallite may be employed in the preparation of magnesium by means of sodium.

Magnesic ammonic chloride, $MgCl_2,NH_4Cl,6OH_2$, is deposited in small rhombic crystals from mixed solutions of magnesic and ammonic chlorides. It is soluble in 6 parts of water.

Magnesic calcic chloride, $2MgCl_2,CaCl_2,12OH_2$, occurs native in deliquescent masses as *tachydrite,* at Stassfurt.

Magnesic bromide, $MgBr_2$, occurs in sea-water and in saline springs. A solution of magnesia in hydrobromic acid deposits needle-shaped crystals of the formula

$MgBr_2,6OH_2$, which when heated behave like the aquate of magnesic chloride. Magnesic bromide forms double salts with the alkaline bromides.

Magnesic iodide, MgI_2, occurs in sea-water and in saline springs, and may be prepared by dissolving magnesia in hydriodic acid. It forms deliquescent crystals which readily decompose when heated.

Magnesic fluoride, MgF_2, occurs native as *sellaïte* in colorless quadratic crystals. It is obtained as a white insoluble powder by digesting magnesia with hydrofluoric acid. By fusion with common salt this powder is converted into crystals having the same form as sellaïte.

Magnesic sodic fluoride, MgF_2,NaF.—This salt is obtained in insoluble, cubical crystals by fusing magnesic chloride with a large excess of sodic fluoride and cooling slowly. It is also formed by digesting magnesia with a solution of sodic fluoride.

COMPOUNDS OF MAGNESIUM WITH OXYGEN AND HYDROXYL.

Magnesic oxide. *Magnesia*, .	MgO.	$Mg{=}O$.
Magnesic hydrate, ...	$MgHo_2$.	$H—O—Mg—O—H$.

MAGNESIC OXIDE (*Magnesia*), MgO, occurs native as *periclase*, a rare mineral found at Monte Somma, near Naples. The natural compound forms regular octahedra, generally of a greenish color, due to the presence of ferrous oxide. It is formed when magnesium burns in the air. It is usually prepared by prolonged ignition of the carbonate, and is thus obtained as a bulky white powder known as *magnesia usta*, or *calcined magnesia*. It is insoluble in water. It possesses a sp. gr. of 3.07, but when very strongly ignited, its sp. gr. is increased to 3.61, the substance becoming at the same time crystalline. By heating magnesia in a current of gaseous hydrochloric acid, it is obtained in crystals identical with those of periclase. It fuses in the oxyhydrogen flame. Magnesia is employed in medicine.

Magnesic hydrate, $MgHo_2$, occurs native as *brucite* in colorless laminated masses. By the addition of sodic or potassic hydrate to solutions of magnesia salts, a gelatinous precipitate is obtained, which, after drying at 100° C. (212° F.), consists of pure magnesic hydrate. It forms a white powder, almost insoluble in water, in solutions of sodic and potassic hydrate, and in aqueous ammonia; readily soluble in solutions of ammonia salts. It absorbs carbonic anhydride from the air. At a low red heat it is decomposed into magnesia and water. The magnesia formed at this low temperature has the property of again taking up water, with evolution of heat, to form the hydrate.

OXY-SALTS OF MAGNESIUM.

Magnesic nitrate, $\begin{matrix}NO_2\\NO_2\end{matrix}Mgo''$, $6OH_2$, forms deliquescent monoclinic prisms, soluble in half their weight of cold water, soluble also in alcohol. The water of crystallization cannot be completely expelled without partial decomposition of the salt.

MAGNESIC CARBONATE, $COMgo''$, occurs native as *magnesite*, sometimes in rhombohedral crystals isomorphous with those of calcite, more frequently massive. The native carbonate generally contains iron and manganese. By precipitating a hot solution of a magnesia salt with potassic or sodic carbonate, and boiling the precipitate with

water as long as any acid carbonate is dissolved, a basic magnesic carbonate of the formula $\mathbf{C}_3Ho_6Mgo''_2(OMgHo)_2 = \left\{\begin{array}{l}\mathbf{C}Ho_2(OMgHo)\\ Mgo\\ \mathbf{C}Ho_2\\ Mgo\\ \mathbf{C}Ho_2(OMgHo)\end{array}\right.$ is obtained. This compound also occurs native as *hydromagnesite* in acicular monoclinic crystals or amorphous masses. By precipitating a magnesia salt with a large excess of sodic carbonate, and boiling with the solution until the precipitate becomes crystalline, a carbonate is obtained having the formula $\mathbf{C}_2Ho_4Mgo''(OMgHo)_2 = \left\{\begin{array}{l}\mathbf{C}Ho_2(OMgHo)\\ Mgo''\\ \mathbf{C}Ho_2(OMgHo)\end{array}\right.$. The pharmaceutical preparation known as *magnesia alba* is a mixture of various complex carbonates of magnesia, obtained by precipitating soluble magnesia salts with sodic carbonate, and varies in composition according to the mode of preparation. It forms a very light, bulky white powder. When *magnesia alba* is suspended in water and the liquid saturated with carbonic anhydride, the powder dissolves with formation of an acid carbonate. On allowing the solution to stand, carbonic anhydride gradually escapes, and a salt of the formula $\mathbf{C}OMgo'',3\mathbf{O}H_2$ separates in fine needles, which when exposed to the air part with their water of crystallization and become opaque. At a very low temperature crystals of a salt having the formula $\mathbf{C}OMgo'',5\mathbf{O}H_2$ are deposited. When the solution of the acid carbonate is evaporated to dryness, anhydrous magnesic carbonate remains as a fine powder, which under the microscope exhibits rhombic forms corresponding to those of arragonite. But if the solution be heated under pressure to 300° C. (572° F.), at the same time allowing the carbonic anhydride to escape gradually, the anhydrous carbonate is obtained in minute rhombohedra, identical with those of native magnesite. Magnesic carbonate is, therefore, isodimorphous with calcic carbonate. When the salt $\mathbf{C}OMgo'',3\mathbf{O}H_2$ is boiled with water it gives off carbonic anhydride, and is converted into a basic salt, whilst when heated in the dry state to 300° C. (572° F.), it is entirely decomposed into carbonic anhydride and magnesia. Native magnesite is not altered by boiling with water, and does not evolve carbonic anhydride at 300° C. It is also only slowly attacked by acids in the cold.

Magnesic dipotassic carbonate, $\begin{array}{l}\mathbf{C}OKo\\ \mathbf{C}OKo\end{array}Mgo'',4\mathbf{O}H_2$, is formed when *magnesia alba* is digested with a solution of hydric potassic carbonate for some time at a temperature of 60–70° C. It forms small rhombic prisms, which are decomposed by water.

Magnesic diammonic carbonate, $\begin{array}{l}\mathbf{C}OAmo\\ \mathbf{C}OAmo\end{array}Mgo'',4\mathbf{O}H_2$, separates in colorless rhombic crystals, when a solution of magnesia salt is added to a large excess of a mixed solution of ammonic carbonate and free ammonia. It is almost insoluble in water.

Magnesic calcic carbonate.—This compound, which, as the mineral *dolomite*, forms entire mountain ranges, is not a true double salt, but an isomorphous mixture of magnesic and calcic carbonates in varying proportions. As *bitter-spar* it occurs crystallized in rhombohedra. It is employed in the preparation of *magnesia alba*.

MAGNESIC SULPHATE, $\mathbf{S}O_2Mgo''$.—A *dihydric magnesic sulphate*, $\mathbf{S}OHo_2Mgo''$, occurs in layers in the salt-beds at Stassfurt as the

mineral *kieserite.* It generally forms granular masses, and is almost insoluble in water, but when allowed to remain long in contact with water gradually dissolves with formation of the salt $SOHo_2Mgo'',6OH_2$. The latter compound occurs native as *epsomite* or Epsom salt, both solid as an efflorescence of fibrous crystals, and in solution in many mineral waters. Magnesic sulphate is deposited from hot concentrated solutions in large transparent rhombic prisms of the above formula $SOHo_2Mgo'',6OH_2$, isomorphous with the corresponding aquates of zincic and nickelous sulphates; but a salt having the same composition is sometimes deposited from cold supersaturated solutions in monoclinic forms isomorphous with those of ferrous sulphate, $SOHo_2Feo'',6OH_2$, with which magnesic sulphate also crystallizes in varying proportions. Above 70° C. (158° F.) it separates from its solutions in monoclinic crystals of the formula $SOHo_2Mgo'',5OH_2$; at 0° C. (32° F.) a salt having the composition $SOHo_2Mgo'',11OH_2$ is deposited. Epsom salt is soluble in four-fifths of its weight of water, still more soluble in water at 100° C. (212° F.), insoluble in alcohol. It has an unpleasant bitter taste. When heated, it fuses in its water of crystallization, which is given off below 150° C. (302° F.), leaving the salt $SOHo_2Mgo''$; this in turn, when heated above 200° C. (392° F.), parts with the elements of water, and is converted into the anhydrous sulphate $SO_2\mathbf{Mgo}''$, which fuses at a red heat without decomposition. The acid salt, *dihydric magnesic disulphate*, $\begin{matrix}SO_2Ho\\SO_2Ho\end{matrix}Mgo''$, crystallizes in six-sided tables from a solution of the anhydrous normal salt in concentrated sulphuric acid. It is instantly decomposed by water. Large quantities of Epsom salt were formerly prepared from dolomite by treating the mineral with sulphuric acid and then separating the soluble Epsom salt from the insoluble calcic sulphate; but at the present day nearly all the Epsom salt is obtained from the kieserite of Stassfurt. The crude kieserite from the upper salt layer, or *Abraumsalz*, is placed in sieves suspended in water. Sodic and magnesic chloride dissolve, the kieserite disintegrates and falls through the meshes of the sieve in a fine powder, whilst earthy impurities are retained by the sieve. The powdered kieserite is then pressed, while wet, into wooden moulds, where it speedily solidifies to a hard mass, owing to the combination of the water with a portion of the kieserite to form Epsom salt, which binds the powder together. The mass is then powdered, and is either brought into the market as kieserite, or is converted first into Epsom salt. Kieserite is employed as a manure, and in the preparation of potassic and sodic sulphate. Epsom salt is used as a purgative. It is also employed in dressing cotton goods and in aniline dyeing.—Magnesic sulphate forms double salts with the alkaline sulphates. *Magnesic dipotassic disulphate*, $\begin{matrix}SO_2Ko\\SO_2Ko\end{matrix}Mgo'',6OH_2$, and *magnesic diammonic disulphate*,

$$\begin{matrix}SO_2Amo\\SO_2Amo\end{matrix}Mgo'',6OH_2,$$

are deposited, from mixed solutions of magnesic sulphate with potassic or with ammonic sulphate, in monoclinic crystals. The potassium salt occurs native at Stassfurt as the mineral *schönite.*

Magnesic orthophosphate, $\begin{matrix}\mathbf{P}OMgo''\\ \mathbf{P}OMgo''\end{matrix}Mgo''$, occurs in bones and the seeds of plants. It is obtained as a white pulverulent precipitate when a solution of trisodic orthophosphate is added to a solution of a magnesia salt. It is almost insoluble in water, but dissolves readily in dilute acids. A double phosphate and fluoride of magnesium having the formula $\mathbf{P}OMgo''\left(\begin{matrix}O\\F\end{matrix}Mg\right)$ occurs in monoclinic crystals as the mineral *wagnerite.*—*Hydric magnesic orthophosphate*, $\mathbf{P}OHoMgo'',7\mathbf{O}H_2$, is deposited in hexagonal needles when dilute solutions of magnesic sulphate and hydric disodic phosphate are mixed. When concentrated solutions are employed, the salt is obtained as an amorphous precipitate which becomes crystalline on standing. It is sparingly soluble in water, and is decomposed by boiling into the normal salt which is deposited and free phosphoric acid which remains in solution.—*Tetrahydric magnesic diorthophosphate* has not been prepared.

Magnesic potassic orthophosphate, $\mathbf{P}OKoMgo'',6\mathbf{O}H_2$, and *magnesic sodic orthophosphate*, $\mathbf{P}ONaoMgo'',9\mathbf{O}H_2$, are obtained in minute crystals by adding to solutions of potassic or sodic dihydric orthophosphate the requisite quantity of magnesia. Both salts are decomposed by washing with water.

Magnesic ammonic orthophosphate, $\mathbf{P}OAmoMgo'',6\mathbf{O}H_2$, separates from putrid urine, and is frequently a constituent of urinary calculi; it occurs also in guano in rhombic crystals as *guanite* or *struvite*. It separates as a crystalline powder when hydric disodic phosphate is added to a mixed solution of a magnesia salt with an ammonia salt and free ammonia. In dilute solutions the precipitate is not formed till after some time; it then attaches itself in small crystals to the sides of the vessel, particularly to parts which have been rubbed with a glass rod in stirring the liquid. It is almost totally insoluble in water, especially in water containing ammonia. When ignited, it is converted into magnesic pyrophosphate:

$$\underset{\text{Magnesic ammonic orthophosphate.}}{2\mathbf{P}OAmoMgo''} = \underset{\text{Magnesic pyrophosphate.}}{\mathbf{P}_2O_3Mgo''_2} + \underset{\text{Ammonia.}}{2\mathbf{N}H_3} + \underset{\text{Water.}}{\mathbf{O}H_2.}$$

Magnesic ammonic phosphate is employed in the estimation both of magnesia and of phosphoric acid.

Magnesic arsenate, $\begin{matrix}\mathbf{As}OMgo''\\ \mathbf{As}OMgo''\end{matrix}Mgo''$, and *hydric magnesic arsenate*,

$$\mathbf{As}OHoMgo'',7\mathbf{O}H_2,$$

are prepared like the corresponding phosphates, and form white precipitates, almost insoluble in water, readily soluble in acids. *Tetrahydric magnesic diarsenate* is soluble in water, but uncrystallizable.

Magnesic ammonic arsenate, $\mathbf{As}OAmoMgo'',6\mathbf{O}H_2$, is prepared like the corresponding phosphate, which it resembles in almost every particular. When dried at 100° C. (212° F.), it parts with $\frac{11}{12}$ of its water of crystallization, yielding the salt—

$$(\mathbf{As}OAmoMgo'')_2,\mathbf{O}H_2, \text{ or } \mathbf{As}_2OHo_2Amo_2Mgo''_2.$$

The rest of the water cannot be expelled without partial decomposition of the salt, a portion of the ammonia being driven off and a portion of the arsenic acid undergoing reduction to arsenious acid. This water is therefore probably to be regarded as water of constitution, as represented in the second of the above formulæ. Magnesic ammonic arsenate is employed in the estimation of arsenic acid.

Magnesic borates.—When magnesia and boric anhydride are fused together at a very high temperature, and the fused mass is allowed to cool slowly, nacreous crystals of *trimagnesic diorthoborate*, $\begin{matrix}\mathbf{B}Mgo''\\ \mathbf{B}Mgo''\end{matrix}Mgo''$, are formed. The same salt with 9 aq. is obtained by precipitating a solution of a magnesia salt with borax. No precipitate is formed in the cold, but on boiling the solution the salt,

$$\begin{matrix}\mathbf{B}Mgo''\\ \mathbf{B}Mgo''\end{matrix}Mgo'',9\mathbf{O}H_2,$$

separates as an amorphous white powder, which dissolves again on cooling. A double dioctoborate and chloride of the formula $\mathbf{B}_{16}O_{18}Mgo''_5\left(\begin{matrix}O\\Cl\end{matrix}Mg\right)_2$, occurs native, in large crystals belonging to the regular system, as *boracite* and massive as *stassfurtite*. The

same compound may be obtained artificially in the crystallized form by fusing magnesic orthoborate with boric anhydride, magnesic chloride, and sodic chloride, allowing the mass to cool slowly, and treating with dilute hydrochloric acid, when the crystals of boracite remain undissolved.

Magnesic silicates.—A number of magnesic silicates occur in nature as minerals. *Peridote* is a *dimagnesic silicate* (*orthosilicate*) of the formula $\mathbf{Si}Mgo''_2$. It occurs in rhombic crystals, generally green-colored, owing to the presence of iron, or in granular masses. *Enstatite* is *monomagnesic silicate* (*metasilicate*) $\mathbf{Si}OMgo''$. It forms monoclinic crystals, which generally contain iron. The following natural magnesic silicates are also known:

Ophite or noble serpentine.	*Trimagnesic disilicate*,	$\mathbf{Si}_2OMgo''_3$.
Meerschaum.	*Tetrahydric dimagnesic trisilicate*, .	$\mathbf{Si}_3O_2Ho_4Mgo''_2$.
Steatite.	*Trimagnesic tetrasilicate*, ...	$\mathbf{Si}_4O_5Mgo''_3$.
Talc.	*Tetramagnesic pentasilicate*, ...	$\mathbf{Si}_5O_6Mgo''_4$.

Numerous natural compound silicates of magnesium with other metals are also known.

COMPOUNDS OF MAGNESIUM WITH SULPHUR AND WITH HYDROSULPHYL.

Magnesic sulphide, $\mathbf{Mg}S''$.—Magnesium is not acted upon by sulphur at the boiling-point of the latter; but when the metal is heated to redness in the vapor of sulphur, magnesic sulphide is formed. It may also be prepared by passing the vapor of carbonic disulphide over red-hot magnesia. It forms a gray or brown, hard, brittle slag. Water decomposes it, yielding a mixture of magnesic hydrate and sulphhydrate. When an excess of sodic sulphide is added to the solution of a magnesium salt, the precipitate which is formed consists not of magnesic sulphide, but of magnesic hydrate.

Magnesic sulphhydrate, $\mathbf{Mg}Hs_2$, has not been prepared pure. It may be obtained in solution by passing sulphuretted hydrogen into water in which magnesia is suspended. On evaporating the solution, sulphuretted hydrogen is given off and magnesia remains.

COMPOUNDS OF MAGNESIUM WITH NITROGEN AND WITH BORON.

Magnesic nitride, $\mathbf{N}_2Mg_3$, is prepared by heating magnesium in nitrogen or gaseous ammonia. The product is an amorphous greenish-yellow mass, which in contact with water, or even in moist air, is decomposed with formation of ammonia and magnesia:

$$\underset{\text{Magnesic nitride.}}{\mathbf{N}_2Mg_3} + \underset{\text{Water.}}{3\mathbf{O}H_2} = \underset{\text{Ammonia.}}{2\mathbf{N}H_3} + \underset{\text{Magnesic oxide.}}{3\mathbf{Mg}O}$$

Magnesic boride, $\mathbf{B}_2Mg_3$, is formed when magnesium is heated with amorphous boron in a closed crucible. It can be obtained, mixed with magnesia, by heating boric anhydride with magnesium. In contact with hydrochloric acid, it evolves boric hydride, $\mathbf{B}H_3$, mixed, however, with a large excess of hydrogen.

COMPOUND OF MAGNESIUM WITH SILICON.

Magnesic silicide, $\mathbf{Si}Mg_2$.—For the method of preparing this compound, see *Silicic hydride*, p. 311.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF MAGNESIUM.—The salts of magnesium with colorless acids are colorless.

The soluble salts have a bitter taste. The hydrates of the *alkalies* and of *baryta* precipitate from solutions of magnesium salts gelatinous magnesic hydrate, insoluble in an excess of the precipitant. When salts of ammonia are present in sufficient quantity, no precipitation occurs with the above reagents *in the cold*, owing to the formation of double salts of ammonium and magnesium, which are not decomposed at ordinary temperatures. For the same reasons the salts of magnesium are only imperfectly precipitated by *ammonia*. *Sodic carbonate* precipitates a basic carbonate; ammonium salts prevent the precipitation. *Ammonic phosphate* gives a white crystalline precipitate of magnesic ammonic phosphate, $\mathbf{P}OAmoMgo'',6\mathbf{O}H_2$, very sparingly soluble in water, insoluble in aqueous ammonia. Magnesium compounds impart no coloration to the non-luminous flame. The spark spectrum of magnesium displays characteristic lines in the green, coincident with lines of the solar spectrum.

ZINC, Zn.

Atomic weight = 65.3. *Molecular weight* = 65.3. *Molecular and atomic volume* $\square\square$. 1 *litre of zinc vapor weighs* 32.65 *criths*. *Sp. gr*. 6.8 *to* 7.2. *Fuses at* 420° C. (788° F.). *Boils at* 1040° C. (1904° F.). *Atomicity* ''. *Evidence of atomicity:*

Zincic chloride, ...	$\mathbf{Zn}''Cl_2$.
Zincic oxide, ...	$\mathbf{Zn}''O$.
Zincic hydrate, ...	$\mathbf{Zn}''Ho_2$.

History.—The ores of zinc were employed by the ancients in the preparation of brass, which they obtained by melting copper with these ores; but zinc was not recognized as a distinct metal till the sixteenth century.

Occurrence.—Zinc is asserted to have been found native near Melbourne, in Australia. It occurs as oxide ($\mathbf{Zn}O$) in *red zinc;* as sulphide ($\mathbf{Zn}S''$) in the mineral *zinc-blende;* as carbonate ($\mathbf{C}OZno''$) in *calamine*, or *zinc-spar;* as silicate ($\mathbf{Si}Zno''_2,\mathbf{O}H_2$) in *siliceous calamine*, or *zinc-glass;* and as double oxides of the general formula $'\mathbf{R}''_2O_2Ro''$ in *franklinite* ($'\mathbf{Fe}''_2O_2Zno''$) and *gahnite* or *zinc-spinelle* ($'\mathbf{Al}''_2O_2Zno''$).

Extraction.—Zinc is obtained from the carbonate, less frequently from the sulphide. Siliceous calamine, red zinc and franklinite are also worked. The first operation in the process of extracting the zinc consists in roasting the ore in order to convert it into oxide. In the case of the carbonate this is effected simply by expulsion of carbonic anhydride; the sulphide is oxidized by the oxygen of the air with evolution of sulphurous anhydride. In roasting the sulphide it is necessary to avoid the formation of zincic sulphate, as this salt would, in the subsequent reducing process, be reconverted into sulphide and thus lost. The roasted ore is then mixed with half its weight of powdered coal, and distilled from fire-clay tubes or from muffles placed in a furnace. At first a finely divided powder known as *zinc-dust*, and consisting of

a mixture of zinc with zincic oxide, frequently also accompanied by cadmium, passes over. Afterwards the liquid metal distils over and is collected in iron receivers, from which it is removed from time to time during the distillation and cast into plates.

Commercial zinc is seldom pure. It generally contains lead, iron, carbon, and sometimes arsenic and cadmium. It may be obtained almost pure by redistillation from clay retorts, the first portions of the distillate, which contain arsenic and cadmium, being rejected, and the operation being interrupted before all the zinc has passed over. The iron, lead, and other less volatile impurities remain in the retort. In order to prepare perfectly pure zinc, the crude metal is dissolved in sulphuric acid, and sulphuretted hydrogen is passed through the acid solution of zincic sulphate. In this way lead, cadmium, and arsenic are precipitated as sulphides. The filtered solution is boiled to expel sulphuretted hydrogen, and the zinc is precipitated as carbonate by the addition of sodic carbonate. The zincic carbonate is converted into oxide by ignition, and the oxide is reduced by distillation from a porcelain retort with pure charcoal prepared from sugar. Any iron which may have been contained in the purified carbonate remains in the retort.

Properties.—Zinc is a white lustrous metal, with a slightly bluish tinge. It has a crystalline, somewhat laminar fracture, and may be obtained in crystals by fusing the metal, allowing it to partially solidify, and then pouring off the still liquid portion. It generally crystallizes in flat hexagonal pyramids, but occasionally exhibits forms belonging to the regular system, especially when it contains traces of copper. At ordinary temperatures it is brittle; between 100° C. (212° F.), and 150° C. (302° F.), it is so malleable and ductile that it may be rolled into plates and drawn into wire; at 205° C. (401° F.) it again becomes so brittle that it may be powdered in a mortar. It may be distilled at a bright red heat. In dry air it preserves its lustre at ordinary temperatures; in moist air it becomes covered with a thin coating of basic carbonate, which preserves it from further action.

Reactions.—1. When heated in air, zinc inflames, emitting a brilliant bluish light, and giving off clouds of zincic oxide. The combustion of zinc is best shown by pressing thin zinc turnings into the form of a cylinder; this, when ignited at a flame, readily burns.

2. Pure zinc is very slowly attacked by dilute sulphuric and hydrochloric acids, but the addition of a few drops of platinic chloride to the liquid causes the zinc to dissolve rapidly, with evolution of hydrogen, the finely divided platinum, which is deposited on the zinc, forming with the latter a voltaic couple. For the same reason commercial zinc, which always contains traces of electronegative metals, is rapidly dissolved by dilute acids. In cold nitric acid the metal dissolves without evolution of gas, the nascent hydrogen being employed in reducing another portion of the acid to ammonia; in hot nitric acid it dissolves with evolution of nitric oxide, nitrous oxide, and free nitrogen, whilst ammonia is also formed. When zinc is acted upon by hot dilute sulphuric acid, or by concentrated sulphuric acid even in the cold, sulphuretted hydro-

gen, formed by the reduction of a portion of the acid, is mixed with the hydrogen which is given off:

$$\underset{\text{Sulphuric acid.}}{5SO_2Ho_2} + 4Zn = \underset{\text{Zincic sulphate.}}{4SO_2Zno''} + \underset{\text{Sulphuretted hydrogen.}}{SH_2} + \underset{\text{Water.}}{4OH_2}.$$

3. Zinc also dissolves in warm solutions of potassic, sodic, and ammonic hydrate, with evolution of hydrogen and formation of a double oxide:

$$\underset{\text{Potassic hydrate.}}{2OKH} + Zn = \underset{\text{Dipotassic zincic oxide.}}{ZnKo_2} + H_2.$$

4. It slowly decomposes aqueous vapor at 100° C. (212° F.):

$$\underset{\text{Water.}}{2OH_2} + Zn = \underset{\text{Zincic hydrate.}}{ZnHo_2} + H_2.$$

Uses.—Zinc, in the form of sheets, is employed for roofing and other purposes in which lightness and the power of resisting the action of the weather are required. In order to preserve iron from rust, the metal is sometimes coated with zinc, in which condition it is known as galvanized iron. Zinc is used in the preparation of plates for voltaic batteries. The finely divided powder obtained in the distillation of zinc, and known as zinc-dust, is frequently employed as a reducing agent in organic chemistry, many oxygenated organic substances, which are unacted upon by all other reducing agents, parting with their oxygen when distilled with zinc-dust. The use of zinc in the desilverization of lead has already been described (p. 448).

COMPOUNDS OF ZINC WITH THE HALOGENS.

ZINCIC CHLORIDE, $ZnCl_2$.

Molecular weight = 136.3. *Molecular volume* $\square\square$.

Zinc foil inflames spontaneously at ordinary temperatures in chlorine gas and burns, forming zincic chloride. The chloride may also be obtained by dissolving zinc in hydrochloric acid, evaporating the solution, and distilling the residue; or by distilling anhydrous zincic sulphate with sodic or calcic chloride. Zincic chloride is a white very deliquescent mass. At ordinary temperatures it is soft like wax; it fuses somewhat above 100° C. (212° F.); at a higher temperature it sublimes in white needles, and may be distilled without decomposition. It is very soluble both in water and in alcohol. The concentrated solution is powerfully caustic: it destroys vegetable fibre, and therefore cannot be filtered through paper. When a little hydrochloric acid is

added to a syrupy solution of zincic chloride, the liquid deposits deliquescent octahedra of the monaquate, $ZnCl_2,OH_2$. The solution of zincic chloride cannot be evaporated without decomposition: hydrochloric acid is given off, and an oxychloride of zinc remains. Oxychlorides of varying composition, consisting of mixtures of ZnHoCl and $ZnHo_2$, are also obtained by heating the concentrated solution of zincic chloride with zincic oxide, and then adding water, when the oxychlorides are precipitated. In the same way, by boiling the solution of the chloride with the requisite quantity of oxide, a plastic mass is obtained which, like the mixture of magnesic chloride and magnesia (p. 508) speedily becomes quite hard.—Owing to its great affinity for water, zincic chloride frequently abstracts the elements of water from organic substances, thus producing new compounds, a property of which application is made in organic research. It is also used as a caustic in medicine, for which purpose it is cast into sticks.—Zincic chloride forms crystalline, deliquescent double salts with the chlorides of the alkalies: for example, *dipotassic zincic chloride*, $ZnCl_2,2KCl$; *disodic zincic chloride*, $ZnCl_2,2NaCl$.

Zincic bromide, $ZnBr_2$, is prepared like the chloride. It crystallizes in very deliquescent prisms, is readily fusible, and may be sublimed in white needles.

Zincic iodide, ZnI_2.—Zinc filings and iodine, when heated together, unite to form the iodide. Zincic iodide is readily fusible, and sublimes in colorless needles. From a concentrated aqueous solution it crystallizes in deliquescent regular octahedra. The concentrated solution takes up oxygen from the air, with liberation of iodine. In like manner, when zincic iodide is heated in air, iodine is given off, and zincic oxide is produced. Zincic iodide combines with the alkaline iodides to form double salts.

Zincic fluoride, ZnF_2, is obtained by dissolving zincic oxide in aqueous hydrofluoric acid. On evaporation, the solution deposits small, shining, rhombic octahedra of the formula $ZnF_2,4OH_2$, sparingly soluble in water. Zincic fluoride forms crystalline double salts with potassic and other fluorides. The potassium salt has the formula $ZnF_2,2KF$.

Zincic silicofluoride, $SiZnF_6,6OH_2$, forms very soluble hexagonal crystals.

COMPOUNDS OF ZINC WITH OXYGEN AND HYDROXYL.

Zincic oxide, ...	ZnO.	$Zn{=}O$.
Zincic hydrate, . . .	$ZnHo_2$.	H—O—Zn—O—H.

ZINCIC OXIDE, ZnO, occurs native, sometimes in hexagonal crystals, more frequently in granular masses, as *red zinc ore*, the color being due to an admixture of manganese. It is formed when zinc is burnt in air (p. 515). On a large scale it is prepared by distilling zinc from earthenware retorts, allowing the zinc vapor to burn as it issues from the retort, and passing the products of combustion through chambers in which the oxide collects. It may also be prepared by igniting the basic carbonate obtained by precipitating the solution of a zinc salt with an alkaline carbonate. The zincic oxide prepared by combustion is a white flocculent substance, and was known to the alchemists as *lana philosophica;* that obtained by the ignition of the carbonate is an amorphous powder. The artificial oxide may be obtained in the hexagonal forms of the

natural variety by igniting it strongly in a current of oxygen. Crystals of zincic oxide are also sometimes found in the cooler parts of the muffles of the zinc furnaces. Zincic oxide has a sp. gr. of 5.6. It is insoluble in water, readily soluble in acids. When heated it assumes a yellow color, changing to white again on cooling. When heated in the oxy-hydrogen flame it does not fuse, but emits a brilliant light, and on cooling continues to phosphoresce for some time in the dark. Zincic oxide is employed as a very permanent white pigment under the name of *zinc white*. As the sulphide of zinc is also white, zinc white does not change color when exposed to sulphurous exhalations, possessing in this respect a marked superiority over white lead.

Zincic hydrate, $ZnHo_2$, is precipitated as a white amorphous powder by the addition of sodic or potassic hydrate, or ammonia, to the solution of a zinc salt. The precipitate is insoluble in water, but soluble in an excess of the precipitant. It may be obtained in a crystalline form by immersing a sheet of zinc, round which a copper wire has been wound, in a solution of the hydrate in ammonia; rhombic prisms of the hydrate are formed upon the surface of the zinc. A saturated solution of the hydrate in caustic potash deposits on standing regular octahedra of the formula $ZnHo_2,OH_2$. When heated, zincic hydrate is readily decomposed into zincic oxide and water.

OXY-SALTS OF ZINC.

Zincic nitrate, $\begin{matrix}NO_2\\NO_2\end{matrix}Zno'',6OH_2$, separates from a concentrated solution of the oxide in nitric acid in deliquescent, colorless, four-sided prisms. It is readily soluble in water and in alcohol. At 36° C. (96.8° F.) it fuses in its water of crystallization, and, when heated to 100° C. (212° F.), parts with water and nitric acid, yielding a basic salt.

Zincic carbonate, $COZno''$, occurs native in translucent rhombohedra as *calamine*. The native carbonate is rarely pure, a portion of the zinc being generally replaced by calcium, iron, and other metals isomorphous with zinc. Zincic carbonate is precipitated when hydric potassic carbonate is added to the solution of a zinc salt. Normal potassic and sodic carbonates precipitate basic zincic carbonates of variable composition. The basic precipitate is insoluble in water and in solutions of potassic and sodic carbonate, but soluble in ammonic carbonate.

ZINCIC SULPHATE (*White vitriol*), SO_2Zno'', is prepared on a large scale by roasting the native sulphide and extracting the mass with water, but is most readily obtained pure by dissolving zinc in sulphuric acid. At ordinary temperatures it crystallizes in large transparent rhombic prisms of the formula $SOHo_2Zno'',6OH_2$, isomorphous with Epsom salt (p. 511), soluble in two-thirds of their weight of water at ordinary temperatures, in one-sixth of their weight of boiling water; insoluble in alcohol. The crystals effloresce slowly in air, and, when heated to 100° C. (212° F.), or exposed *in vacuo* over sulphuric acid, part with 6 aq., leaving the salt $SOHo_2Zno''$, which is converted at a temperature of 240° C. (464° F.) into anhydrous zincic sulphate (SO_2Zno'') and water. At temperatures above 40° C. (104° F.) solutions of zincic

sulphate deposit monoclinic crystals having the formula $SOHo_2Zno''$,-$5OH_2$, also isomorphous with the corresponding magnesium salt. When the anhydrous salt is heated to a high temperature it gives off sulphurous anhydride and oxygen, yielding a basic salt, a hot saturated solution of which deposits on cooling lustrous laminæ of the formula $SO(OZnHo)_4$. The same compound may be obtained by boiling a solution of zincic sulphate with zincic oxide. At a white heat the anhydrous sulphate is converted into zincic oxide. Zincic sulphate forms double sulphates with the sulphates of the alkalies, *zincic dipotassic disulphate,* $\begin{matrix}SO_2Ko\\SO_2Ko\end{matrix}Zno'',6OH_2$, and *zincic diammonic disulphate,* $\begin{matrix}SO_2Amo\\SO_2Amo\end{matrix}Zno'',6OH_2$, which are isomorphous with and closely resemble the corresponding magnesium compounds. Mixed solutions of zincic and magnesic sulphates deposit crystals containing the two salts in variable proportions.—Zincic sulphate is employed in medicine and in calico printing.

Zincic orthophosphate.—The normal or *trizincic* salt, $\begin{matrix}POZno''\\POZno''\end{matrix}Zno'',4OH_2$, is formed when hydric disodic phosphate is added to a solution of a zinc salt. It is a white precipitate, which, when deposited from cold solutions, is gelatinous, but becomes crystalline on standing or on heating.—The acid phosphates have not been prepared.

Zincic silicate.—A *dizincic silicate,* $SiZno''_2$, occurs native in hexagonal prisms as *willemite.* It may be obtained artificially in the crystallized form by passing silicic fluoride over zincic oxide heated almost to whiteness, or by the action of zincic fluoride on silicic anhydride.—The same compound with 1 aq., $SiZno''_2,OH_2$—perhaps to be regarded as $SiO(OZnHo)_2$—occurs in rhombic crystals as the mineral *zinc glass or siliceous calamine.*

COMPOUNDS OF ZINC WITH SULPHUR.

ZINCIC SULPHIDE, ZnS'', occurs native as *zinc blende*, either crystallized in forms belonging to the regular system, or massive. The color of the mineral varies from a pale yellow, in the purer specimens, to a brown or black in the massive variety, due to the presence of iron and other impurities. Zincic sulphide is occasionally found in hexagonal prisms as the mineral *wurtzite.* It is obtained as a white amorphous precipitate when sulphuretted hydrogen is passed through a solution of zincic acetate. From neutral solutions of zinc salts with mineral acids the zinc is only partially precipitated by sulphuretted hydrogen, and in acid solutions no precipitate is produced. All zinc salts, however, are completely precipitated by the addition of alkaline sulphides or sulphhydrates to their solutions. The precipitated zincic sulphide is insoluble in water and in acetic acid, but readily soluble in mineral acids with evolution of sulphuretted hydrogen. Zincic sulphide is difficultly fusible. When the amorphous sulphide is heated to a very high temperature in a current of sulphuretted hydrogen, or sulphurous anhydride, it sublimes in colorless hexagonal crystals identical with those of wurtzite.

Trizincic dipotassic tetrasulphide, $S_4Zn_3K_2$.

$$K—S—Zn—S—Zn—S—Zn—S—K.$$

This compound is obtained by fusing together 1 part of zincic sulphide, 24 parts of potassic carbonate, and 24 parts of sulphur, at a red heat for ten minutes. On extract-

ing the cooled mass with water, the double sulphide remains in the form of colorless transparent laminæ, which may be boiled with water without decomposition.—The corresponding sodium compound $S_4Zn_3Na_2$, may be obtained in a similar manner, and forms a pale flesh-colored crystalline powder.

Zincic pentasulphide, S_5Zn, is obtained as a white precipitate by the addition of potassic pentasulphide to the neutral solution of a zinc salt. It assumes a pale yellow color on drying, and, when heated with exclusion of air, gives off sulphur, and is converted into the monosulphide.

COMPOUNDS OF ZINC WITH THE PENTAD ELEMENTS.

Zincic nitride, N_2Zn_3.—When zinc ethyl (see Organic Chemistry) is acted upon by gaseous ammonia, ethylic hydride is evolved, and *zinc diamine* is formed:

$$\underset{\text{Zinc ethyl.}}{\mathbf{Zn}(C_2H_5)_2} + \underset{\text{Ammonia.}}{2\mathbf{N}H_3} = \underset{\text{Zinc diamine.}}{\mathbf{Zn}(NH_2)_2} + \underset{\text{Ethylic hydride.}}{2\left\{\begin{matrix}\mathbf{C}_2H_5 \\ H\end{matrix}\right.}.$$

The zinc diamine thus obtained is a white amorphous powder, which is decomposed by water with formation of ammonia and zincic hydrate:

$$\underset{\text{Zinc diamine.}}{\mathbf{Zn}(NH_2)_2} + \underset{\text{Water.}}{2\mathbf{O}H_2} = \underset{\text{Zincic hydrate.}}{\mathbf{Zn}Ho_2} + \underset{\text{Ammonia.}}{2\mathbf{N}H_3}.$$

When zinc diamine is heated to low redness in absence of air, ammonia is evolved, and zincic nitride remains as a green powder:

$$\underset{\text{Zinc diamine.}}{3\mathbf{Zn}(NH_2)_2} = \underset{\text{Zincic nitride.}}{\mathbf{N}_2Zn_3} + \underset{\text{Ammonia.}}{4\mathbf{N}H_3}.$$

In contact with water zincic nitride is decomposed with great evolution of heat, yielding ammonia and zincic oxide.

Zincic phosphide, P_2Zn_3, is prepared by heating finely divided zinc in the vapor of phosphorus. An impure compound is obtained by heating a mixture of phosphoric anhydride, zincic oxide, and charcoal. Zincic phosphide forms a steel-gray metallic mass, which dissolves in hydrochloric acid with evolution of phosphoretted hydrogen.

Zincic arsenide, As_2Zn_3, is formed with incandescence when zinc and arsenic are heated together in the proportions required by the formula. It is a gray, brittle metallic mass, which, when acted upon by dilute hydrochloric acid, evolves pure arseniuretted hydrogen (p. 367).

Zincic antimonide, Sb_2Zn_3, is obtained as a white crystalline metallic mass by fusing together 57 parts of antimony and 43 parts of zinc. By allowing the fused compound partially to solidify, and pouring off the still liquid portion, it may be obtained in well-formed hexagonal prisms. When treated with hydrochloric acid, it evolves a mixture of hydrogen and antimoniuretted hydrogen (p. 380).—A *dizincic diantimonide* of the formula $'Sb''_2Zn_2$, crystallizing in rhombic octahedra, is prepared by fusing 68.5 parts of antimony with 31.6 parts of zinc.

General Properties and Reactions of the Compounds of Zinc.—The salts of zinc are colorless when the constituent acid is so. They have an astringent metallic taste, and are poisonous. From their solutions *caustic alkalies* and *ammonia* precipitate white zincic hydrate, soluble in excess of the precipitant. *Alkaline carbonates* precipitate a basic carbonate, soluble in ammonic carbonate, but not in excess of potassic or sodic carbonate. *Baric carbonate* does not precipitate solutions of zinc salts. *Sulphuretted hydrogen* gives no precipitate in acid solutions, except in the case of salts of organic acids in solutions acidulated

with these acids; *ammonic sulphide* precipitates white hydrated zincic sulphide. *Potassic ferrocyanide* gives a white precipitate of zincic ferrocyanide. Heated on charcoal in the reducing flame of the blowpipe, zinc compounds yield a characteristic incrustation of zincic oxide, yellow while hot, white when cold. If this incrustation be moistened with cobaltous nitrate and again heated, it assumes a fine green color (Rinmann's green). The salts of zinc do not color the non-luminous flame. The spark spectrum of zinc shows characteristic lines in the red and in the blue.

BERYLLIUM, Be.

(Sometimes termed *Glucinum*, symbol G.)

Atomic weight = 9. *Probable molecular weight* = 9. *Sp. gr.* 2.1. *Fuses at a red heat. Atomicity* ''. *Evidence of atomicity:*

Beryllic chloride, ...	$\mathbf{Be}''Cl_2$.
Beryllic oxide, ...	$\mathbf{Be}''O$.
Beryllic hydrate, ...	$\mathbf{Be}''Ho_2$.

History.—Beryllic oxide was prepared by Vauquelin in 1798. Wöhler first isolated the metal in 1828.

Occurrence.—Beryllium occurs in combination in a few rare minerals. *Beryl,* a native double silicate of beryllium and aluminium of the formula $\mathbf{Si}_6O_6('Al'''_2O_6)^{vi}Beo''_3$, is the most abundant source of the beryllium compounds. This mineral crystallizes in hexagonal prisms, generally opaque, and of a greenish tint. The precious stone *emerald* is a transparent beryl of a brilliant green color; bluish-green specimens, when transparent, are known as *aquamarine,* and are also employed as gems. The mineral *phenacite* is a silicate of beryllium having the formula $\mathbf{Si}Beo''_2$.

Preparation.—Metallic beryllium is prepared by passing the vapor of beryllic chloride along with a current of hydrogen over heated sodium, and afterwards fusing the metal thus obtained in a crucible under sodic chloride.

Properties.—Beryllium is a lustrous silver-white malleable metal of sp. gr. 2.1. It fuses below the melting point of silver. When fused in air it becomes covered with a thin coating of oxide, which checks further oxidation; but when heated in a finely divided state it inflames, burning with a very brilliant light. It does not decompose water, even at 100° C. (212° F.). Dilute hydrochloric acid dissolves it readily in the cold, with evolution of hydrogen, but dilute sulphuric acid does not attack it till heated, whilst nitric acid, even when hot and concentrated, acts upon it only very slowly. It is not attacked by ammonia, but dissolves readily in caustic potash with evolution of hydrogen.

COMPOUNDS OF BERYLLIUM WITH THE HALOGENS.

Beryllic chloride, $\mathbf{Be}Cl_2$.—*Molecular weight* = 80. *Molecular volume* $\square\square$.—The anhydrous chloride is obtained in lustrous, colorless, needle-shaped crystals by passing chlorine over a heated mixture of

beryllic oxide and charcoal. It is readily fusible and volatile. The crystals deliquesce rapidly when exposed to air, and, when thrown into water, dissolve with a hissing sound, evolving heat. The aqueous solution, which may also be obtained by dissolving the oxide in hydrochloric acid, deposits, by spontaneous evaporation over sulphuric acid, colorless crystals of the formula $\mathbf{Be}Cl_2,4\mathbf{O}H_2$, from which the water of crystallization cannot be expelled without decomposition of the salt.

Beryllic bromide, $\mathbf{Be}Br_2$, and *Beryllic iodide*, $\mathbf{Be}I_2$, are both obtained in the form of colorless needles by the direct union of their elements.

Beryllic fluoride, $\mathbf{Be}F_2$.—The anhydrous salt is not known. The solution of beryllic hydrate in hydrofluoric acid deposits on evaporation an amorphous mass, which when further heated gives off water and hydrofluoric acid, being partially converted into oxide. It forms double fluorides with the fluorides of the alkali metals.

COMPOUNDS OF BERYLLIUM WITH OXYGEN AND HYDROXYL.

Beryllic oxide, *Beryllia*, .	$\mathbf{Be}O$.	$Be{=}O$.
Beryllic hydrate, ...	$\mathbf{Be}Ho_2$.	$H{-}O{-}Be{-}O{-}H$.

Beryllic oxide or *Beryllia*, $\mathbf{Be}O$.—This oxide is prepared from the mineral beryl, a beryllic aluminic silicate (p. 521). The finely powdered mineral is fused with three parts of anhydrous potassic carbonate, and the cooled mass is treated with concentrated sulphuric acid, the excess of acid being expelled by heating. On extracting with water, the sulphates of beryllium, aluminium, and potassium dissolve, whilst the silica remains and may be filtered off. The solution is evaporated until a crust begins to form on the surface. On standing, the greater portion of the alumina crystallizes out as potash alum, $\left.\begin{array}{l}\mathbf{S}O_2Ko{-}\\ \mathbf{S}O_2{-}\\ \mathbf{S}O_2{-}\\ \mathbf{S}O_2Ko{-}\end{array}\right]({}'Al'''_2O_6)^{vi},24\mathbf{O}H_2$, the beryllia remaining in solution. A fresh crop of alum crystals may be obtained by the further exaporation of the mother liquor from the first crop. The filtered liquid from the second crop of crystals is then poured into an excess of a warm solution of ammonic carbonate, and the whole is allowed to remain for some days in a stoppered bottle, agitating from time to time. The precipitate, consisting of alumina and ferric oxide, is filtered off, and the beryllia is precipitated from the solution, either as basic carbonate by protracted boiling, or as hydrate by acidulating with hydrochloric acid and afterwards rendering alkaline with ammonia. By ignition the carbonate or hydrate is converted into oxide. Thus prepared beryllia forms a white bulky amorphous powder of sp. gr. 3.08, resembling magnesia in appearance. It is insoluble in water, and, after being strongly ignited, does not dissolve in dilute acids. Like magnesia, it becomes crystalline by exposure to a very intense heat.

Beryllic hydrate, $\mathbf{Be}Ho_2$, is obtained as a gelatinous precipitate when ammonia is added to a solution of a beryllium salt. After drying at 100° C. it forms a bulky white

powder, which at a higher temperature is converted into the oxide. It is insoluble in water, soluble in solutions of caustic potash, caustic soda, and ammonic carbonate, but insoluble in ammonia. If the solution in caustic potash be diluted and boiled, the beryllic hydrate is reprecipitated. From the solution in ammonic carbonate a precipitate of a basic beryllic carbonate separates on boiling. Beryllic hydrate dissolves in a boiling solution of ammonic chloride with formation of beryllic chloride and with liberation of ammonia.

OXY-SALTS OF BERYLLIUM.

Beryllic nitrate, $\begin{matrix}NO_2\\NO_2\end{matrix}Beo'',3OH_2$, forms deliquescent crystals, readily soluble in alcohol. At a temperature of 250° C. it is completely converted into oxide.

Beryllic carbonate.—The precipitate produced in solutions of beryllium salts by alkaline carbonates is a basic beryllic carbonate of the formula $CHo(OBeHo)_3,3OH_2$. This salt dissolves in water containing carbonic anhydride, and the solution, when evaporated over sulphuric acid in an atmosphere of carbonic anhydride, deposits crystals of the normal carbonate, $COBeo'',4OH_2$. These, on exposure to the air, spontaneously part with carbonic anhydride and are re-converted into the basic salt.

Beryllic sulphate, $SOHo_2Beo'',3OH_2$, crystallizes from aqueous solutions in quadratic octahedra, which are soluble in their own weight of water at ordinary temperatures, and effloresce on exposure to the air. The water of crystallization is expelled at 110° C., leaving the salt $SOHo_2Beo''$. This salt is stable at 150° C., but at a higher temperature the water of constitution is expelled and the anhydrous salt SO_2Beo'' remains. At a red heat the anhydrous salt is converted into beryllia. From solutions containing free sulphuric acid, beryllic sulphate crystallizes in large efflorescent monoclinic prisms of the formula $SOHo_2Beo'',6OH_2$, isomorphous with those of Epsom salt.* Mixed solutions of beryllic and magnesic sulphates deposit crystals containing the two metals in variable proportions.

Beryllic orthophosphate.—A *hydric beryllic phosphate*, $POHoBeo'',3OH_2$, is obtained as a white amorphous precipitate when hydric disodic phosphate is added to the solution of a beryllium salt. When the sodic phosphate is added to a solution containing beryllic nitrate and ammonic chloride, the triple salt, *disodic diammonic beryllic phosphate*, $P_2O_2Nao_2(NH_4O)_2Beo'',7OH_2$, is precipitated as a white crystalline powder.

Beryllic silicate, $SiBeo''_2$, occurs native in hexagonal crystals as *phenacite*.

COMPOUND OF BERYLLIUM WITH SULPHUR.

Beryllic sulphide, BeS'', is formed as a gray infusible mass when beryllium is heated in sulphur vapor. Alkaline sulphides precipitate only beryllic hydrate from solutions of beryllium salts.

General Properties and Reactions of the Compounds of Beryllium.—The salts of beryllium with colorless acids are colorless; they have a sweet, slightly astringent taste and an acid reaction. *Caustic alkalies, ammonia*, and *ammonic sulphide* precipitate white flocculent beryllic hydrate, in the case of the last precipitant with evolution of sulphuretted hydrogen. The precipitate is soluble in excess of caustic alkali, but not in excess of ammonia. Beryllic hydrate is soluble in *ammonic carbonate*, and may thus be separated from alumina, along

* Marignac, however, doubts whether these salts are really isomorphous.

with which it is usually precipitated in analysis. Beryllium salts do not color the non-luminous flame. The spark spectrum contains two characteristic lines in the blue.

CHAPTER XXXIV.

DYAD ELEMENTS.

SECTION III.

CADMIUM, Cd.

Atomic weight = 112. *Molecular weight* = 112. *Molecular and atomic volume* ☐☐. 1 *litre of cadmium vapor weighs* 56 *criths. Sp. gr.* 8.6. *Fuses at* 320° C. (608° F.). *Boils at* 860° C. (1580° F.). *Atomicity* ″. *Evidence of atomicity:*

Cadmic chloride, ...	$Cd''Cl_2$.
Cadmic oxide, ...	$Cd''O$.

History.—Cadmium was discovered independently and almost simultaneously by Stromeyer and by Hermann in 1817.

Occurrence.—Cadmium occurs in small quantities in many zinc ores. A fibrous zinc blende found at Przibram in Bohemia contains as much as from 2 to 3 per cent. of cadmium. The rare mineral *greenockite* is a sulphide of cadmium (CdS'').

Preparation.—In the process of extracting zinc from ores containing cadmium, the latter metal distils over first, and is for the most part oxidized by the air in the receivers. By distilling these first portions with powdered coal at as low a temperature as possible, cadmium is obtained almost pure. In order to purify it thoroughly, it is dissolved in dilute sulphuric or hydrochloric acid and precipitated from the acid solution by sulphuretted hydrogen, the zinc remaining in solution. The cadmic sulphide is redissolved in concentrated hydrochloric acid, and the cadmium is precipitated from the solution by an excess of ammonic carbonate, which dissolves any arsenic and copper that may be present. The cadmic carbonate is converted by ignition into oxide, which by distillation with a tenth of its weight of powdered coal yields the pure metal.

Properties.—Cadmium is a white lustrous metal, with a fibrous fracture. When pure it is very malleable and ductile. It loses its lustre by exposure to the air, and when heated in air burns, giving off a brown smoke of cadmic oxide. Dilute sulphuric and hydrochloric acids dissolve it slowly with evolution of hydrogen. Nitric acid rapidly dissolves it. Zinc precipitates it in the metallic form from the solution of its salts.

COMPOUNDS OF CADMIUM WITH THE HALOGENS.

Cadmic chloride, $CdCl_2$.—A solution of the metal or of the oxide in hydrochloric acid deposits on evaporation colorless prisms of the composition $CdCl_2,2OH_2$, which effloresce when exposed to the air. The water of crystallization may be expelled by heat without decomposition of the salt. The anhydrous chloride fuses below a red heat, and at a higher temperature may be sublimed in colorless laminæ. One hundred parts of water at 20° C. dissolve 141 parts of the anhydrous salt, and the solubility scarcely varies with the temperature. It forms a number of crystalline double chlorides with the alkaline and many other chlorides.

Cadmic bromide, $CdBr_2$, is prepared by digesting cadmium with bromine and water. On evaporation the solution yields efflorescent acicular crystals of the formula $CdBr_2$-$4OH_2$, which on heating become anhydrous. At a higher temperature the salt fuses and sublimes in colorless laminæ. It forms double bromides with the bromides of the alkalies and alkaline earths.

Cadmic iodide, CdI_2, is prepared like the bromide. It crystallizes from water in fusible hexagonal plates. When heated it is decomposed with evolution of iodine. One hundred parts of water at 20° C. (68° F.) dissolve 93 parts of the salt; at 100° C. (212° F.), 133 parts. It is also soluble in alcohol. If forms numerous double iodides with the iodides of other metals. Cadmic iodide is employed in photography.

COMPOUNDS OF CADMIUM WITH OXYGEN AND HYDROXYL.

Cadmic oxide, . . .	CdO.	$Cd{=}O$.
Cadmic hydrate, . .	$CdHo_2$.	$H{-}O{-}Cd{-}O{-}H$.

Cadmic oxide, CdO, may be prepared like the oxide of zinc by the combustion of the metal. It is thus obtained as a brown amorphous powder. When cadmic nitrate is ignited the oxide remains in the form of microscopic octahedra, which by reflected light appear blue-black, by transmitted light brown. It is insoluble in water, readily soluble in acids. It is infusible even at a white heat. When heated on charcoal before the blowpipe, it is reduced, the metal at the same time volatilizing and burning with formation of a brown incrustation of cadmic oxide on the charcoal.

Cadmic hydrate, $CdHo_2$, is obtained by precipitating the solution of a cadmium salt with potassic or sodic hydrate, and drying the precipitate at 100° C. (212° F.). It forms a white powder, insoluble in water and in solutions of potassic and sodic hydrate; readily soluble in ammonia and in acids. It absorbs carbonic anhydride from the air. At 300° C. (572° F.) it is converted into oxide.

OXY-SALTS OF CADMIUM.

Cadmic nitrate, $\begin{matrix}NO_2\\NO_2\end{matrix}Cdo'',4OH_2$, crystallizes in deliquescent prisms, soluble in alcohol.

Cadmic carbonate.—A precipitate approximating in composition to that of the normal

salt, $COCdo''$, is obtained by adding in the cold a solution of a cadmium salt to an excess of an alkaline carbonate. The precipitate formed at a higher temperature, or with a smaller quantity of alkaline carbonate, is a basic salt of varying composition.

Cadmic sulphate, SO_2Cdo'', is deposited from its solutions by spontaneous evaporation at ordinary temperatures in large colorless monoclinic crystals of the formula $3SO_2Cdo'',8OH_2$. A boiling solution containing an excess of sulphuric acid deposits warty crystals of a salt SO_2Cdo'',OH_2. The anhydrous salt is soluble in less than twice its weight of water at ordinary temperatures; somewhat more soluble at 100° C. (212° F.). The normal salt is converted by heating into a basic compound of the formula $SO_2(OCdHo)_2$, sparingly soluble in water and crystallizing in pearly scales. Cadmic sulphate is employed in medicine.

COMPOUND OF CADMIUM WITH SULPHUR.

CADMIC SULPHIDE, CdS'', occurs native in yellow hexagonal prisms as the rare mineral *greenockite.* It is obtained as an amorphous powder of a pure yellow color when a solution of a cadmium salt is precipitated with sulphuretted hydrogen or with an alkaline sulphide. It is soluble in concentrated nitric and hydrochloric acids, and in hot dilute sulphuric acid. It fuses at a white heat, and solidifies on cooling in micaceous scales. By fusing the precipitated sulphide with potassic carbonate and sulphur, extracting the cooled mass with water, or by passing the vapor of sulphur over cadmic oxide heated to the highest possible temperature, cadmic sulphide may be obtained in hexagonal crystals.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF CADMIUM.—The salts of cadmium with colorless acids are colorless. *Caustic alkalies* precipitate from solutions of the salts white cadmic hydrate, insoluble in excess of the precipitant. *Ammonia* gives the same precipitate, readily soluble however in excess. *Ammonic carbonate* precipitates cadmic carbonate, insoluble in excess. *Sulphuretted hydrogen* precipitates from a hydrochloric acid solution yellow cadmic sulphide, insoluble in ammonic sulphide and in potassic cyanide, but soluble in hot dilute sulphuric acid. Heated on charcoal before the blowpipe, cadmium compounds give a brown incrustation of cadmic oxide. Cadmium compounds do not color the non-luminous flame. The spark spectrum displays characteristic lines in the red, green, and blue.

MERCURY, Hg.

Atomic weight = 200. *Molecular weight* = 200. *Molecular and atomic volume* $\square\square$. 1 *litre of mercury vapor weighs* 100 *criths. Sp. gr.* 13.59. *Fuses at* —39.5° C. (—39.1° F.). *Boils at* 357.25° C. (675.05° F.) (Regnault). *Atomicity* ″, *also a pseudo-monad. Evidence of atomicity:*

Mercuric chloride, ...	$Hg''Cl_2$.
Mercuric oxide, ...	$Hg''O$.
Mercurous chloride, ...	$'Hg'_2Cl_2$.
Mercurous oxide, ...	$'Hg'_2O$.

History.—Mercury has been known from almost the earliest historic times.

Occurrence.—Mercury is found native in minute globules disseminated through its ores. It occurs in combination as chloride and iodide, and also with gold and silver in the form of amalgams. Its most abundant ore is mercuric sulphide or *cinnabar*. The most important mines are those of Idria in Carniola, Almaden in Spain, Napa Valley in California, and at Wolfsstein and Landsberg in the Bavarian Palatinate.

Extraction.—At Idria the ore—a mixture of cinnabar with earthy matters—is placed on the top of a perforated arch, under which the furnace is situated. After closing the aperture through which the ore has been introduced the furnace is lighted. The flame, along with an excess of air which is allowed to enter by openings constructed for that purpose, plays through the perforations of the arch upon the ore, oxidizing the sulphur to sulphurous anhydried, and volatilizing the mercury. The products of combustion pass through stone chambers, in which the mercury condenses, and thence into a tower, through which a stream of water trickles, removing the last traces of mercury from the escaping gases. At Almaden, the mercury vapor, instead of passing into stone chambers, is condensed in a series of stoneware bottles termed *aludels*, open both at top and bottom, and so arranged that the neck of each fits into the bottom of the next.

A furnace, in which from 50 to 60 tons of ore can be distilled in one operation, can be filled and the charge worked off in a day; but four or five days must be allowed to elapse before the furnace is sufficiently cool to be recharged. In order to obviate this loss of time, a continuous process has been devised in which the ore, along with charcoal, is introduced from time to time at the top of the furnace whilst the ashes are withdrawn at the bottom.

In the Bavarian Palatinate the ore is mixed with lime and distilled from iron retorts. Mercury passes over, and a mixture of calcic sulphide and sulphate remains. In Bohemia the ore is distilled with smithy-scales.

Mercury obtained by any of the above processes is freed from mechanical impurities by filtering through linen. It is generally sent into the market in iron bottles.

Preparation of Pure Mercury.—Commercial mercury is generally contaminated with small quantities of foreign metals which it holds in solution. The presence of these impurities is manifested by a diminution of the fluidity of the mercury, accompanied by a tendency to adhere to glass or porcelain; a globule of pure mercury runs rapidly and coherently over a clean inclined surface of porcelain; but when the mercury is impure the globule becomes considerably elongated in its course, and generally leaves behind it on the porcelain a dark-colored track of oxide in which traces of the metal are retained. Mercury may be freed from these impurities by distillation, the surface of the metal being covered during the operation with a thick layer of iron-filings to diminish spirting. A very pure product may be obtained by conducting the distillation in a Sprengel vacuum. Mercury may also be purified by agitating it with dilute nitric acid, or by leaving it in shallow vessels in contact with the acid, when the impurities are dissolved first. Mercury is also very effectively purified by leaving it for several days under a layer of concentrated sulphuric acid. Pure mercury ought to leave no residue when dissolved in nitric acid, evaporated, and ignited.

Properties.—Mercury is a silver-white, very lustrous metal. It is liquid at ordinary temperatures, but solidifies at —39.5° C. to a tin-white, malleable, and sectile mass, crystallizing in regular octahedra. It contracts during solidification. Mercury volatilizes sensibly at ordinary temperatures: a piece of gold leaf suspended in a closed vessel over mercury becomes in course of time white and silvery, owing to the absorption of the mercurial vapor by the gold. Mercury boils at 357.25° C. (675.05° F.), yielding a colorless vapor. Pure mercury undergoes scarcely any alteration in air at ordinary temperatures, though a very thin film of mercurous oxide is formed on the surface; but at a temperature near to its boiling point it gradually absorbs oxygen with formation of red mercuric oxide. Hydrochloric acid, even when hot and concentrated, is without action upon mercury. Sulphuric acid does not attack it in the cold; but the hot concentrated acid dissolves it with evolution of sulphurous anhydride. When the metal is present in excess, and the temperature is not allowed to rise to the boiling point of the mixture, a mercurous salt is formed; an excess of acid leads to the formation of a mercuric salt. Cold dilute nitric acid dissolves it, yielding mercurous nitrate; when an excess of the metal is boiled with the dilute acid a basic mercurous nitrate is obtained. Hot concentrated nitric acid in excess dissolves it with evolution of nitric oxide and formation of mercuric nitrate. When a rapid stream of water from a tap is directed from a height of three or four inches upon the surface of a large mass of mercury, bubbles of mercury are formed and float on the surface of the water. These transmit blue light through the thin metallic film, and deposit on bursting a minute globule of mercury. When mercury is triturated with sugar, grease, and various other substances, it is obtained in a very finely divided state, the union of the particles of the metal being prevented by the interposition of the foreign substance. This process is known as the "deadening" of the mercury. In the case of gray mercurial ointment, which is prepared

by this method, the mercury forms nearly uniform globules having a diameter of 0.001 to 0.004 mm. The vapor of mercury when inhaled acts as a poison, producing salivation. The finely divided mercury when taken internally has a similar action; but liquid mercury has been swallowed without noticeable ill effects.

Uses.—Mercury is invaluable to the physicist and the chemist. Many important physical observations could not have been made without the aid of apparatus of which mercury forms an essential part. The chemist employs mercury in collecting and measuring gases which are soluble in water, and also for the preparation of the mercurial compounds. It is further used in silvering mirrors, in extracting gold and silver from their ores by the amalgamation process, and in medicine.

Amalgams.

The alloys of the various metals with mercury are known as amalgams. Some amalgams are formed by the direct union of their constituents, the combination either taking place spontaneously at ordinary temperatures, or requiring the aid of heat. Gold, silver, tin, sodium, and many other metals may be thus directly amalgamated. In other cases an indirect process must be resorted to. If the metal is more electro-positive than mercury, it may frequently be amalgamated by immersing it in the solution of a salt of mercury; in this way an amalgam of copper may be prepared. Other indirect methods of amalgamation are: the electrolysis of a solution of the metal, employing mercury as the negative electrode, and the action of an amalgam of sodium upon the solution.

Potassium amalgam.—Potassium and mercury combine with considerable rise of temperature, but without incandescence. The amalgam is solid when it contains 1 part of potassium to 96 parts of mercury, but liquid when the proportion of mercury rises to 140 parts. The solid amalgam crystallizes in cubes.

Sodium amalgam.—Sodium and mercury combine violently at ordinary temperatures, the process being attended with a hissing noise and vivid incandescence. An amalgam containing 100 parts of mercury to 1 of sodium is viscid; with 80 parts of mercury, pasty; with 40 parts, solid; and with 30 parts, hard.

The amalgams of potassium and sodium when brought in contact with water evolve hydrogen. Sodium amalgam is employed as a reducing agent in organic chemistry (p. 425). It is also used in the extraction of gold and silver (p. 449).

Iron amalgam.—Iron may be amalgamated by rubbing its clean surface with sodium amalgam.

Ammonium amalgam.—See p. 235.

Copper amalgam.—When copper is immersed in a solution of nitrate of mercury, the mercury is deposited on the surface of the copper. By treating finely divided or precipitated copper in this way, and then triturating it under warm water with the requisite quantity of mercury, an amalgam of copper may be obtained. Copper amalgam containing 30 per cent. of copper is hard enough to scratch tin, but has the re-

markable property of becoming soft and plastic by heating to 100° C. (212° F.) and kneading in a mortar, recovering its hardness in the course of a few hours. As it has the same density in the soft as in the hard state, it may be employed to stop cavities, which it exactly fills on solidifying. In this way it has been used for stopping teeth.

Cadmium amalgam possesses the same plastic properties as the above, and is also employed in dentistry.

Tin amalgam.—Tin dissolves in mercury with absorption of heat. According to the relative proportions the amalgam is either liquid, or solid and crystalline. Tin amalgam is employed in silvering mirrors.

COMPOUNDS OF MERCURY WITH THE HALOGENS.

a. Mercurous Compounds.

MERCUROUS CHLORIDE, *Calomel*, $'\mathbf{Hg}'_2Cl_2$.—*Molecular weight* = 471.—This compound occurs in lustrous quadratic crystals or crystalline crusts as the rare mineral *horn-quicksilver*. It is precipitated by the addition of hydrochloric acid or a soluble chloride to a solution of mercurous nitrate. It is also precipitated when a solution of mercuric chloride is saturated with sulphurous anhydride and the liquid is warmed to 70° C. (158° F.) or 80° C. (176° F.). Calomel is generally prepared, however, in the dry way by subliming together 4 parts of mercuric chloride with 3 parts of metallic mercury. The sublimation is performed in a cast-iron cylinder, and the calomel vapor is passed into the upper part of a large brick chamber, where it condenses in a fine powder, as in the process of preparing flowers of sulphur. The product must be thoroughly washed with large quantities of warm water in order to remove any unaltered mercuric chloride. When the vapor is allowed to condense on a cold surface, the mercurous chloride is obtained as a fibrous crystalline mass of sp. gr. 7.1. Mercurous chloride assumes a gray tint under the action of light, owing to the separation of metallic mercury. When heated it sublimes without fusing. It possesses a vapor density only half of that required by the formula $'\mathbf{Hg}'_2Cl_2$; but investigation has shown that the supposed vapor of calomel consists of a mixture of the vapors of mercuric chloride and mercury, which recombine on cooling:

$$\underset{\text{Mercurous chloride.}}{'\mathbf{Hg}'_2Cl_2} = \underset{\text{Mercuric chloride, 2 vols.}}{\mathbf{Hg}Cl_2} + \underset{\text{2 vols.}}{\mathbf{Hg}.}$$

It is insoluble in water, in alcohol, and in dilute acids in the cold. By boiling with hydrochloric acid it is converted into mercuric chloride, which dissolves, and metallic mercury. In contact with caustic potash it blackens, owing to the formation of mercurous oxide.—Calomel is much used in medicine.

Mercurous bromide, $'\mathbf{Hg}'_2Br_2$, is prepared by precipitating a solution of mercurous nitrate with hydrobromic acid or with a soluble bromide, and also by subliming a mix-

ture of mercuric bromide and metallic mercury. It closely resembles the chloride in its properties, and, like that compound, possesses a vapor density only half of that required by its formula.

Mercurous iodide, $'\mathbf{Hg}'_2I_2$, may be obtained by triturating 10 parts of mercury with 6.7 parts of iodine, adding sufficient alcohol to moisten the mass. The product must be washed with alcohol in order to remove any mercuric iodide. It forms a yellowish-green powder, which fuses at 290° C. (554° F.), yielding a black liquid. It sublimes below this temperature, and by careful sublimation may be obtained in yellow rhombic crystals. These, when heated to 70° C. (158° F.), assume a red color, which deepens as the temperature rises, till at 220° C. (428° F.) it attains to a deep garnet-red. This change of color is not accompanied by any change in composition, and the crystals recover their original color on cooling. When quickly heated, mercurous iodide is decomposed into mercuric iodide and metallic mercury, and the same change takes place gradually at ordinary temperatures. It is only sparingly soluble in water. In contact with a solution of potassic iodide it is decomposed into mercuric iodide, which dissolves with formation of potassic mercuric iodide, and metallic mercury.

Mercurous fluoride, $'\mathbf{Hg}'_2F_2$, is prepared by dissolving freshly precipitated mercurous carbonate in hydrofluoric acid and evaporating the solution. It forms small yellow crystals, which are partially decomposed by pure water with separation of mercurous oxide. When the dry fluoride is heated in a glass vessel, mercury sublimes and the glass is corroded.

b. Mercuric Compounds.

MERCURIC CHLORIDE, *Corrosive sublimate*, $\mathbf{Hg}Cl_2$.—*Molecular weight* = 271. *Molecular volume* □□.—This compound is formed when mercury is heated in an excess of chlorine; also when mercuric oxide is dissolved in hydrochloric acid, or mercury in aqua-regia. It is generally prepared by heating a mixture of mercuric sulphate and common salt; the mercuric chloride sublimes and condenses as a colorless, transparent, crystalline mass in the upper part of the vessel. A small quantity of manganic dioxide is added to the mercuric sulphate in order to oxidize any mercurous salt which may be present. Mercuric chloride crystallizes from its aqueous solution in long colorless rhombic prisms, having a sp. gr. of 5.4. It fuses at 265° C. (509° F.) and boils at 295° C. (563° F.). It is soluble in from 14 to 15 parts of water at ordinary temperatures, in 2 parts of water at 100° C. (212° F.). It also dissolves in 3 parts of alcohol and in 4 parts of ether. Mercuric chloride is exceedingly stable, dissolving in concentrated nitric acid and sulphuric acid without decomposition. On heating the sulphuric acid solution the mercuric chloride sublimes out of the concentrated acid unchanged. Mercuric chloride is a violent poison. It is employed in medicine and as an antiseptic for anatomical preparations.—Mercuric chloride forms the following crystallizable double salts with the alkaline chlorides:

$$\mathbf{Hg}Cl_2KCl,\mathbf{O}H_2;\ \mathbf{Hg}Cl_2,2KCl,\mathbf{O}H_2;\ 2\mathbf{Hg}Cl_2,KCl,2\mathbf{O}H_2;$$
$$\mathbf{Hg}Cl_2,2NaCl;\ 2\mathbf{Hg}Cl_2,2NaCl,3\mathbf{O}H_2;\ \mathbf{Hg}Cl_2,\mathbf{N}H_4Cl;$$
$$\mathbf{Hg}Cl_2,2\mathbf{N}H_4Cl,\mathbf{O}H_2$$

(*sal alembroth*). It also combines with hydrochloric acid to form the crystallized compounds $\mathbf{Hg}Cl_2,HCl$ and $2\mathbf{Hg}Cl_2,HCl$, both of which, on exposure to air, effloresce and part with the whole of their hydrochloric acid.—By boiling a solution of mercuric chloride with mercuric oxide, or by adding to the solution a quantity of caustic alkali insufficient for

complete precipitation, various oxychlorides of mercury, many of which are crystallizable, may be obtained. The compound

$$\mathbf{Hg}_4O_3Cl_2 = Cl—Hg—O—Hg—O—Hg—O—Hg—Cl$$

forms lustrous golden-yellow scales.

Mercuric bromide, $\mathbf{Hg}Br_2$, is obtained by the direct union of mercury with an excess of bromine. It is less soluble than the chloride, and crystallizes from water in lustrous laminæ, from alcohol in rhombic needles or prisms. It sublimes readily.

MERCURIC IODIDE, $\mathbf{Hg}I_2$, is prepared by triturating 10 parts of mercury with 13 parts of iodine, adding sufficient alcohol to moisten the mass; or by mixing solutions of 10 parts of mercuric chloride and 12¼ parts of potassic iodide. The product obtained by the direct combination of iodine with mercury is a brilliant red crystalline powder; that prepared by precipitation is at first of a pure yellow, but speedily becomes red on standing. It is insoluble in water, readily soluble in alcohol or in solutions of potassic iodide and of mercuric chloride, yielding colorless solutions. From the alcoholic solution it is deposited in red quadratic octahedra. When mercuric iodide is heated to 150° C. (302° F.) it suddenly changes its color to yellow; at 238° C. (460.4° F.) it fuses to a yellow liquid and volatilizes in yellow lustrous rhombic crystals, which on standing or sometimes even during the process of cooling, are converted into aggregates of the red crystals. This change into the red modification, which is accompanied by evolution of heat, takes place instantaneously on scratching the yellow crystals. Mercuric iodide yields with potassic and ammonic iodides double salts of the formulæ $2(\mathbf{Hg}I_2,KI),3\mathbf{O}H_2$ and $2(\mathbf{Hg}I_2,\mathbf{N}H_4I),3\mathbf{O}H_2$, which crystallize in yellow prisms.

Mercuric fluoride, $\mathbf{Hg}F_2$.—Mercuric oxide added to hydrofluoric acid is converted into a yellow crystalline powder consisting of *mercuric oxyfluoride,* $\mathbf{Hg}FHo$, and the solution yields on evaporation orange-colored crystals of the same compound. An excess of water decomposes the oxyfluoride, even in the cold, into hydrofluoric acid and mercuric oxide. By repeatedly treating the oxyfluoride with concentrated hydrofluoric acid, mercuric fluoride is obtained as a white crystalline mass of the formula $\mathbf{Hg}F_2,2\mathbf{O}H_2$. The same compound is formed when mercuric oxide is added to a large excess of hydrofluoric acid containing 50 per cent. HF. When heated to 50° C. (122° F.) it is converted into the oxyfluoride. In contact with water it is decomposed into hydrofluoric acid and mercuric oxide.

COMPOUNDS OF MERCURY WITH OXYGEN.

Mercurous oxide, ...	$'\mathbf{Hg}'_2O$.	$\left.\begin{matrix}Hg\\ \vert\\ Hg\end{matrix}\right>O.$
Mercuric oxide, ...	$\mathbf{Hg}O$.	$Hg=O.$

MERCUROUS OXIDE, $'\mathbf{Hg}'_2O$.—This compound is obtained as a black powder by precipitating a mercurous salt with potassic or sodic hydrate. By the action of light it is decomposed into mercuric oxide and metallic mercury; for this reason it must be washed and dried in the dark. It

is decomposed in the same manner when heated to 100° C. (212° F.). Acids dissolve it, yielding the mercurous salts.

MERCURIC OXIDE, HgO, is formed as a red crystalline powder when mercury is heated in air to a temperature near its boiling-point. It is most conveniently prepared by thoroughly triturating mercuric nitrate with an equal weight of mercury and cautiously heating the mixture until acid fumes cease to be evolved. When prepared on a large scale by this method, it is sometimes obtained in small brick-red rhombic crystals, having a sp. gr. of 11.136. It is precipitated as a yellow amorphous powder when potassic or sodic hydrate is added to the solution of a mercuric salt. Mercuric oxide is not quite insoluble in water, to which it imparts an alkaline reaction and a metallic taste. When carefully heated it assumes a deeper color, gradually passing into black, but recovers its original tint on cooling. At a red heat it is totally decomposed into mercury and oxygen. When heated with bodies which take up oxygen it oxidizes them: a mixture of mercuric oxide and sulphur explodes with great violence on heating. Mercuric oxide is gradually blackened by exposure to light, owing to a partial decomposition.

OXY-SALTS OF MERCURY.

a. Mercurous Salts.

MERCUROUS NITRATE.—When mercury is dissolved in cold dilute nitric acid the solution deposits colorless monoclinic tables or prisms of the normal salt *tetrahydric mercurous dinitrate*, $\begin{matrix} NOHo_2 \\ NOHo_2 \end{matrix}('Hg'_2O_2)''$. It dissolves without decomposition in water containing nitric acid, but in contact with an excess of pure cold water it is decomposed, yielding the basic salt *hydric mercurous nitrate*, $NOHo('Hg'_2O_2)''$, as a yellow crystalline powder which is converted on boiling with water into mercuric nitrate and metallic mercury. Other basic mercurous nitrates are known, some of which crystallize well. Thus when the crystals of the normal salt are heated with their mother liquor in contact with an excess of mercury, the solution deposits on cooling colorless, lustrous, non-efflorescent, rhombic prisms of *hydric dimercurous trinitrate*, $N_3O_5Ho('Hg'_2O_2)''_2$. If, on the other hand, the crystals of the normal salt are left for some time in the cold in contact with the mother liquor along with an excess of mercury, lustrous triclinic prisms of *tetrahydric pentamercurous hexanitrate*, $N_6O_8Ho_4('Hg'_2O_2)''_5$, are formed.—The normal mercurous nitrate forms numerous crystallizable double salts with the nitrates of other metals.

Mercurous chlorate, $\left\{\begin{matrix} OCl \\ O \end{matrix}\right. \!\!\!\begin{matrix} \\ ('Hg'_2O_2)'' \end{matrix} \left\{\begin{matrix} O \\ OCl \end{matrix}\right.$, is obtained in colorless rhombic prisms by dissolving freshly precipitated mercurous oxide in chloric acid. When heated to 250° C. it decomposes into mercuric chloride, mercuric oxide, and oxygen.

Mercurous perchlorate, $\left\{\begin{matrix}\mathrm{OCl}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{O}\end{matrix}\right.({}'\mathrm{Hg}'_2\mathrm{O}_2)'',6\mathrm{OH}_2$, is obtained in colorless deliquescent needles by dissolving mercurous oxide in an aqueous solution of perchloric acid.

Mercurous bromate, $\left\{\begin{matrix}\mathrm{OBr}\\ \mathrm{O}\\ \mathrm{O}\\ \mathrm{OBr}\end{matrix}\right.({}'\mathrm{Hg}'_2\mathrm{O}_2)''$, is deposited in colorless laminæ when solutions of mercurous nitrate and potassic bromate are mixed. An excess of water decomposes it with formation of a basic salt.

Mercurous carbonate, $\mathrm{CO}({}'\mathrm{Hg}'_2\mathrm{O}_2)''$, is precipitated as a yellow powder when a solution of mercurous nitrate is poured into an excess of hydric potassic carbonate or hydric sodic carbonate. Mercurous carbonate decomposes at 130° C. (266° F.) into carbonic anhydride, mercury, and mercuric oxide.

Mercurous sulphate, $\mathrm{SO}_2({}'\mathrm{Hg}'_2\mathrm{O}_2)''$, is obtained as a white crystalline mass by gently heating sulphuric acid with an excess of mercury. If the temperature be raised too high, a mercuric salt is formed at the same time. Mercurous sulphate is also deposited in minute colorless prisms when dilute sulphuric acid is added to a solution of mercurous nitrate. It is only slightly soluble in water. When heated it fuses to a reddish-brown liquid which solidifies on cooling to a crystalline mass. With careful heating it may be sublimed.

b. Mercuric Salts.

MERCURIC NITRATE, $\begin{matrix}\mathrm{NO}_2\\ \mathrm{NO}_2\end{matrix}\mathrm{Hgo}''$.—This salt is prepared by boiling mercury with an excess of nitric acid until a portion of the liquid, when removed and tested with a solution of common salt, yields no precipitate. The normal salt is, on account of its deliquescent nature, very difficult to obtain in a crystallized state. When the solution is evaporated over sulphuric acid, large deliquescent crystals of *dihydric dimercuric tetranitrate,* $\mathrm{N}_4\mathrm{O}_7\mathrm{Ho}_2\mathrm{Hgo}''_2$, are obtained. A hydrated normal salt is deposited in tabular crystals of the formula $\mathrm{N}_2\mathrm{O}_4\mathrm{Hgo}'',8\mathrm{OH}_2$, when a solution of the nitrate in nitric acid is cooled to —15° C; the crystals fuse at ordinary temperatures. Mercuric nitrate has a great tendency to form basic salts: a solution of an excess of mercuric oxide in hot, moderately strong nitric acid, deposits on cooling colorless rhombic crystals of *tetrahydric dimercuric dinitrate,* $\mathrm{N}_2\mathrm{OHo}_4\mathrm{Hgo}''_2$. When this salt, or any of the normal salts, is treated with cold water, a still more basic salt, *dihydric trimercuric dinitrate,* $\mathrm{N}_2\mathrm{OHo}_2\mathrm{Hgo}''_3$, is formed as a white powder, and this, when boiled with an excess of water, gradually parts with all its acid and is converted into mercuric oxide.

Mercuric carbonate.—The mercuric carbonates are basic compounds of ill-defined character and uncertain composition. They form brown amorphous powders.

Mercuric sulphate, $\mathrm{SO}_2\mathrm{Hgo}''$.—This salt is prepared by heating mercury with one and a half times its weight of sulphuric acid until the excess of acid is expelled. It is thus obtained as a white crystalline

mass, which when heated turns first yellow and afterwards brown, but becomes white again on cooling. At a red heat it decomposes into mercury, oxygen, and sulphurous anhydride. When treated with a small quantity of water it forms white crystals of *dihydric mercuric sulphate*, $SOHo_2Hgo''$, but an excess of water decomposes it, especially on boiling, into free sulphuric acid and a yellow insoluble basic salt, *trimercuric sulphate*, $SHgo''_3$, formerly known as *turpeth mineral* (*turpetum minerale*).

Mercuric orthophosphate, $\begin{matrix} POHgo'' \\ POHgo'' \end{matrix} Hgo''$.—This salt is precipitated as a heavy white insoluble powder when ordinary sodic phosphate is added to a solution of mercuric nitrate. Mercuric chloride cannot be substituted for the nitrate.

Borates and *silicates* of mercury have not been prepared.

COMPOUNDS OF MERCURY WITH SULPHUR.

Mercuric sulphide, $'Hg'_2S''$, is precipitated as a black powder by pouring a dilute solution of mercurous nitrate into a dilute solution of ammonic sulphhydrate. It may also be prepared by treating freshly precipitated calomel with ammonic sulphhydrate. It is a very unstable compound, and is decomposed even by a gentle heat into mercury and mercuric sulphide.*

MERCURIC SULPHIDE, *Cinnabar*, *Vermilion*, HgS''.—This compound occurs native in red hexagonal crystals, and also in granular masses, as the mineral *cinnabar*, constituting the most abundant ore of mercury. By triturating mercury with sulphur, the sulphide is obtained as a black amorphous powder; the product thus formed is known in pharmacy as *Aethiops mineralis*. The same black modification is obtained by precipitating a mercuric salt with an excess of sulphuretted hydrogen. When the black amorphous sulphide is sublimed with exclusion of air, it is converted into the crystalline variety, which condenses on a cold surface, generally as a red fibrous mass, but sometimes in distinct crystals having the form of a native compound. By digesting with warm solutions of alkaline persulphides, the black sulphide is also converted into the red sulphide. The finely ground red sulphide is employed as a pigment under the name of *vermilion*, and is prepared on a large scale in the wet way by the following method: 100 parts of mercury are thoroughly triturated with 38 parts of flowers of sulphur, and the mass is then digested for several hours at a temperature of 45–50° C. (113–122° F.) with a solution of 25 parts of caustic potash in 150 parts of water, renewing the water as fast as it evaporates. As soon as the vermilion has attained the proper shade the operation is interrupted and the product is quickly washed with water, as by the further action of the potash the color changes to brown. Vermilion prepared in the wet way has a finer shade than that obtained by sublimation. Mercuric sulphide is insoluble in hydrochloric, nitric, and sulphuric acids, but soluble in aqua-regia and in hydriodic acid. Ammonic sulphide does not dissolve it, but it is soluble in potassic and sodic sulphides in

* According to some chemists the so-called mercurous sulphide is merely a mixture of mercuric sulphide and mercury.

presence of free alkali. The solution in potassic sulphide deposits colorless needles of *mercuric dipotassic sulphide*, $HgKs_2,5OH_2$ The sodium compound has the formula $HgNas_2,8OH_2$. Both compounds are decomposed by an excess of water with separation of black sulphide. By digesting the black sulphide with a solution of mercuric chloride, or by fusing the dry sulphide with an excess of mercuric chloride and extracting the mass with water, *trimercuric disulphodichloride*, $\begin{matrix}HgCl\\HgCl\end{matrix}Hgs'' = Cl{-}Hg{-}S{-}Hg{-}S{-}Hg{-}Cl$, is obtained as a white powder which is amorphous when prepared in the wet way, and crystalline when prepared in the dry way. The same substance is formed as a white precipitate when sulphuretted hydrogen is passed into a solution of mercuric chloride, but is converted by an excess of sulphuretted hydrogen into black sulphide. Mercuric sulphide forms numerous other double compounds with mercuric salts.

COMPOUND OF MERCURY WITH NITROGEN.

Mercuric nitride, $N_2Hg''_3$, is formed when mercuric oxide, prepared by precipitation and dried at a low temperature, is heated to 100° C. in a current of ammonia:

$$\underset{\text{Mercuric oxide.}}{3HgO} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Mercuric nitride.}}{N_2Hg''_3} + \underset{\text{Water.}}{3OH_2}.$$

The product is treated with dilute nitric acid to free it from any unaltered mercuric oxide. It forms a dark-brown powder, which explodes with great violence by heat, friction, or contact with concentrated sulphuric acid. By cautiously heating with caustic alkalies it is decomposed without detonation, yielding ammonia and sublimed mercury.

AMMONIACAL MERCURY COMPOUNDS.

These compounds are derived from the ordinary ammonium salts by the replacement of one or more atoms of hydrogen in the latter by mercury. The mercury may be present either as Hg'' or as $'Hg'_2$, and each of these dyad radicals may either replace two atoms of hydrogen in a single ammonium molecule, or may replace two atoms of hydrogen in two different ammonium molecules; in the latter case uniting the two ammonium groups to a single molecule. The free mercury-ammoniums have not been prepared.

a. Mercurosammonium Compounds.

Mercurosammonic chloride, $NH_2'Hg'_2Cl$, is obtained as a black insoluble powder by the action of aqueous ammonia on mercurous chloride:

$$\underset{\text{Mercurous chloride.}}{'Hg'_2Cl_2} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Mercurosammonic chloride.}}{NH_2'Hg'_2Cl} + \underset{\text{Ammonic chloride.}}{NH_4Cl}.$$

Gaseous hydrochloric acid decomposes it, yielding mercurous chloride and ammonic chloride:

$$\underset{\text{Mercurosammonic chloride.}}{NH_2'Hg'_2Cl} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Mercurous chloride.}}{'Hg'_2Cl_2} + \underset{\text{Ammonic chloride.}}{NH_4Cl}.$$

When heated, it first gives off ammonia and nitrogen, and afterwards mercurous chloride and metallic mercury.

Mercurosammonic nitrate, $NO_2(N^vH_2'Hg'_2O)$.—This compound, known as *Mercurius solubilis Hahnemanni*, is precipitated in the form of a black powder when aqueous am-

monia is added to a solution of mercurous nitrate. It is with difficulty obtained in a state of purity, and is generally mixed with metallic mercury.

Mercurosodiammonic dichloride, $\left.\begin{matrix}NH_3ClHg\\NH_3ClHg\end{matrix}\right\}$, is formed as a black powder by the action of gaseous ammonia upon mercurous chloride. When heated, or when exposed to the air, it evolves ammonia, leaving mercurous chloride.

b. Mercurammonium Compounds.

Dimercurammonic oxide, $\begin{matrix}NHg''_2\\NHg''_2\end{matrix}O$.—When mercuric oxide is treated with concentrated ammonia, *dimercurammonic hydrate* is obtained as a pale yellow powder having the formula $NHg''_2Ho,2OH_2$. By sudden heating or by friction it deflagrates without explosion. When heated to 80° C. (176° F.) in a current of ammonia it gives off water, leaving the pure hydrate NHg''_2Ho, which at 100° C. (212° F.) parts with the elements of water, and is converted into the oxide. Dimercurammonic oxide is a brown powder, which on heating or by friction explodes violently.

Mercurammonic chloride, $NH_2Hg''Cl$.—This compound, known as *infusible white precipitate,* is prepared by precipitating a solution of mercuric chloride with an excess of ammonia:

$$\underset{\text{Mercurous chloride.}}{HgCl_2} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Mercurammonic chloride.}}{NH_2Hg''Cl} + \underset{\text{Ammonic chloride.}}{NH_4Cl.}$$

At a temperature below a red heat it is decomposed without fusion, yielding ammonia, nitrogen, and mercurous chloride. Water decomposes it, slowly in the cold and quickly on heating, with formation of ammonic chloride and an aquate of *dimercurammonic chloride,* NHg''_2Cl,OH_2.

Dimercurammonic chloride, NHg''_2Cl, is obtained as a yellow powder by the action of alcoholic hydrochloric acid on dimercurammonic oxide (see above), or by treating mercurammonic chloride with water (see preceding compound). When heated to 300° C. (572° F.) it decomposes into metallic mercury, mercurous chloride, and nitrogen.

Mercuridiammonic dichloride, $\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}Hg''$.—This compound, known as *fusible white precipitate,* is obtained by adding a solution of mercuric chloride to a boiling solution of ammonic chloride and ammonia as long as the precipitate which is at first formed continues to dissolve. The liquid on cooling deposits colorless regular dodecahedra, which fuse when heated, and then decompose, yielding nitrogen, ammonia, mercurous and mercuric chlorides, and ammonic chloride.

Hydroxydimercurammonic iodide, $NHHg''(Hg''Ho)I$, is formed by the action of an excess of aqueous ammonia upon mercuric iodide:

$$\underset{\text{Ammonia.}}{4NH_3} + \underset{\text{Mercuric iodide.}}{2HgI_2} + \underset{\text{Water.}}{OH_2} = \underset{\text{Hydroxydimercurammonic iodide.}}{NHHg''(Hg''Ho)I} + \underset{\text{Ammonic iodide.}}{3NH_4I.}$$

It is most readily obtained by adding ammonia to a solution of mercuric potassic iodide containing an excess of potassic hydrate. This liquid, which is known as *Nessler's solution,* is employed in testing for minute traces of ammonia. When the quantity of ammonia is too small to yield with this reagent a precipitate of hydroxydimercurammonic iodide, it manifests its presence by a yellow coloration. Hydroxydimercurammonic iodide is a reddish-brown powder, which fuses when heated, and at a higher temperature decomposes with a violent explosion.

CHARACTERISTIC PROPERTIES AND REACTIONS OF THE COMPOUNDS OF MERCURY.—The normal salts of mercury with colorless acids are colorless; some of the basic salts are yellow. The soluble salts have an acid metallic taste, and act as irritant poisons. If a strip of copper be introduced into a solution of any mercury compound, metallic mercury is deposited on the copper. All compounds of mercury, when heated in a test-tube with dry sodic carbonate, yield a gray sublimate consisting of minute globules of mercury.

a. *Mercurous salts,* when in solution, yield with *caustic alkalies* black mercurous oxide. *Ammonia* precipitates black mercurosammonium compounds (p. 536). *Sulphuretted hydrogen* and *ammonic sulphide* precipitate black mercurous sulphide, insoluble in nitric acid, soluble in aqua regia. *Hydrochloric acid* precipitates white mercurous chloride, and *potassic iodide* green mercurous iodide. *Stannous chloride* precipitates mercurous chloride, which is converted by an excess of the stannous chloride into gray metallic mercury.

b. *Mercuric salts* give, with solutions of caustic alkalies, a yellow precipitate of mercuric oxide. *Ammonia* precipitates a white mercurammonium compound (p. 537). *Sulphuretted hydrogen* gives a white precipitate, which passes through red to black, and then consists of mercuric sulphide; this precipitate is insoluble in nitric and in hydrochloric acid, soluble in aqua-regia. *Potassic iodide* precipitates salmon-red mercuric iodide, soluble both in mercuric chloride and in potassic iodide. *Stannous chloride* precipitates mercurous chloride, which is then converted into metallic mercury.

The mercury compounds give no flame-coloration. The spark spectrum displays bright lines in the green and blue.

COPPER, Cu.

Atomic weight = 63.2. *Probable molecular weight* = 63.2. *Sp. gr.* 8.9. *Fuses at* 1330° C. (2426° F.). *Atomicity* ″, *also a pseudo-monad. Evidence of atomicity:*

Cupric chloride, ...	$\mathbf{Cu}''Cl_2$.
Cupric oxide, ...	$\mathbf{Cu}''O$.
Cuprous chloride, ...	$'\mathbf{Cu}'_2Cl_2$.
Cuprous oxide, ...	$'\mathbf{Cu}'_2O$.

History.—Copper has been known from prehistoric times. Owing to its occurring in the native state, it formed the material for tools and weapons in early ages when the metallurgical processes necessary for the extraction of iron from its ores were unknown.

Occurrence.—Native copper occurs in various localities, particularly in the neighborhood of Lake Superior, where it is sometimes found in enormous masses. In the Minnesota Mine, in 1857, a mass of copper weighing 420 tons was found. In combination it occurs as cuprous oxide, $'\mathbf{Cu}'_2O$, in *red copper ore* or *ruby-ore;* much more rarely as cupric oxide, $\mathbf{Cu}O$, in *tenorite.* It also occurs as cuprous sulphide, $'\mathbf{Cu}'_2S''$, in *copper glance;* as cupric sulphide, $\mathbf{Cu}S''$, in *indigo copper;* as a double sulphide of copper and iron, diferric cuprous tetrasulphide, $\left\{\begin{matrix}\mathbf{Fe}S'' \\ \mathbf{Fe}S''\end{matrix}\right.('Cu'_2S''_2)''$, in *copper pyrites;* as basic carbonates in *malachite,* $\mathbf{C}O(OCu''Ho)_2$, and *azurite,* $\left\{\begin{matrix}\mathbf{C}HoCuo'' \\ Cuo'' \\ \mathbf{C}HoCuo''\end{matrix}\right.$. It also occurs in minute quantity in sea-weed, and as a necessary constituent of the blue blood of various marine animals, such as the cuttle-fish. In this blue blood

the copper is present in the form of *hæmocyanin*, a complex organic compound, which acts as a carrier of oxygen and thus exercises the same functions which hæmoglobin, an organic substance containing iron, exercises in the red blood of the higher animals. In the arterial blood the hæmocyanin is blue, in the venous blood it becomes colorless, a change identical with that which occurs when a copper salt passes from the higher or cupric to the lower or cuprous state of oxidation.

Extraction.—The process of *copper-smelting*, by which copper is obtained from its ores, varies with the nature of these ores; thus, the oxides or carbonates may be reduced directly by heating with charcoal, but in the case of the sulphides the ore must be first roasted in order to convert the sulphur into sulphurous anhydride. The process employed in England is as follows: The mixed ore, which consists of copper pyrites and cupric carbonates, together with iron pyrites and siliceous impurities, and which ought to contain about 13 per cent. of copper, is first calcined on the bed of a reverberatory furnace. Air is admitted through air-holes, and plays along with the flame of the furnace upon the surface of the ore, which is turned over from time to time by means of long rakes introduced through doors opening on the bed. In this way the sulphides of iron and copper are partially converted into oxides. The next process consists in the fusion of the calcined ore with *metal slag*, a siliceous slag obtained in a subsequent operation, to which fluorspar is also frequently added in order to increase its fusibility. The fusion is performed on the bed of a reverberatory furnace, the so-called *ore-furnace*, the temperature of which is much higher than that of the calcining furnace. The oxides of copper which are present react with the unaltered sulphide of iron, yielding oxide of iron, which is taken up by the slag, and cuprous sulphide, which combines with the excess of ferrous sulphide to form the so-called *coarse metal*, the latter collecting under the slag in a depressed basin on the hearth of the furnace, whence it can be drawn off through a tap-hole. The coarse metal has very much the composition of ordinary copper pyrites. The slag, which contains all the siliceous matters from the ores, together with a great portion of the iron, and is almost free from copper, is known as *ore-furnace slag*. The coarse metal is next powdered and calcined, by which means a partial oxidation is again effected, and the mass is then fused along with the *refinery slag* from the final process. The decomposition which takes place is the same as that which occurs in the fusion of the calcined ore, except that in the present case practically the whole of the iron is oxidized and passes into the slag, whilst the copper collects at the bottom of the furnace in the form of cuprous sulphide, $'\mathbf{Cu}'_2S''$, known as *fine metal* (also *white metal*). The slag, which is termed *metal slag*, contains about 3 per cent. of copper, and is employed as above described in the fusion of the calcined ore. The fine metal is then roasted in a reverberatory furnace. A portion of the cuprous sulphide is thus oxidized to cuprous oxide, which then reacts with another portion of cuprous sulphide yielding metallic copper:

$$\underset{\text{Cuprous oxide.}}{2'\mathbf{Cu}'_2O} + \underset{\text{Cuprous sulphide.}}{'\mathbf{Cu}'_2S''} = 6Cu + \underset{\text{Sulphurous anhydride.}}{\mathbf{SO}_2}.$$

The copper thus obtained is covered with black blisters, and is therefore known as *blister copper*. It contains small quantities of iron, arsenic, lead, and other metals. It is refined by fusion on the bed of a furnace in a current of air. In this way the foreign metals are oxidized and combine with the siliceous materials of which the bed of the furnace is composed to form a slag, which is skimmed off. This slag, which is very rich in copper, is known as *refinery slag*, and is employed as above described. The refined copper is known as *dry copper*. It contains a certain quantity of cuprous oxide, which would render it brittle when cold. It is therefore subjected to a process of *toughening*. For this purpose the surface of the fused metal, after the removal of the slag, is covered with a layer of powdered anthracite (charcoal was formerly used) and a pole of green birch or oak is thrust into it. The reducing gases, evolved by the destructive distillation of the wood in contact with the hot metal, effect the conversion of the cuprous oxide into copper, and this reduction is further facilitated by the violent agitation of the entire mass caused by the escaping gases, the particles of carbon being thus carried down under the surface and brought in contact with every part of the metal. This process is known as *poling*. After continuing this treatment for twenty minutes the pole is withdrawn, and a sample of the metal is removed and cast in an ingot mould; the bar of copper is cut half through and then broken by bending in a vise; an examination of the fracture enables the refiner to say whether the required degree of toughness has been attained. If this point has been passed, the metal is *over-poled* and less tenacious; it may be toughened again by fusion for a short time in contact with air. The nature of the change which occurs in over-poling is not perfectly understood; by some chemists the loss of tenacity is attributed to a too complete reduction of the cuprous oxide, others believe that foreign oxides are reduced at the close of the operation, and that the metals from these become alloyed with the copper.

Large quantities of copper are now obtained by extraction *in the wet way*. The quantity of iron pyrites burnt in the sulphuric acid works of this country amounts to 500,000 tons per annum, and this substance contains on an average 3 per cent. of copper, the whole of which remains in the burnt pyrites. It would be impossible, by the ordinary processes of copper-smelting, to extract this small quantity, but it has been found that by roasting the burnt pyrites with from 12 to 15 per cent. of common salt, and lixiviating the mass with water, the whole of the copper is obtained in solution in the form of cupric chloride, and may be precipitated as metallic copper by scrap iron.

Commercial copper generally contains traces of various other metals, especially silver, arsenic, and iron. Pure copper is best obtained by heating the pure oxide in a current of hydrogen, or by electrolyzing a solution of pure cupric sulphate.

Properties.—Copper is a lustrous metal with a peculiar red color. This color can be seen in its full intensity only when the light, before reaching the eye, has been reflected several times from the surface of the metal (p. 399). Copper crystallizes in cubes or octahedra. It is one of the most tenacious of metals, and is very malleable and ductile;

it may be beaten into thin leaf, or drawn into fine wire. Very thin copper leaf transmits a greenish-blue light. In dry air, copper tarnishes only very slightly at ordinary temperatures, but in contact with water or in moist air it becomes coated with basic carbonate. When heated in air or in oxygen it is converted superficially into black oxide, which may be readily detached in scales. Copper is quite insoluble in dilute hydrochloric or sulphuric acid as long as air is excluded; but with admission of air, or in contact with some more electro-negative metal, such as platinum, it gradually dissolves. Finely divided copper slowly dissolves in boiling hydrochloric acid with evolution of hydrogen. Concentrated sulphuric acid is without action upon it at ordinary temperatures; but with the hot concentrated acid cupric sulphate is formed and sulphurous anhydride evolved (p. 261). Dilute nitric acid attacks it violently, even in the cold, with formation of cupric nitrate and evolution of nitric oxide (p. 224). Ammonia dissolves the metal slowly in presence of air. Iron, zinc, phosphorus, and many other readily oxidizing substances, precipitate copper in the metallic state from the solutions of its salts.

Uses.—Copper is employed for a great variety of purposes in the arts, and is especially valuable where great flexibility combined with tenacity is required. It is used for bell-wire and for the fire boxes of locomotive boilers, its high conductivity for heat peculiarly fitting it for the latter purpose. The electric conductivity of copper is higher than that of any other known metal, with the exception of silver; hence copper wire is extensively employed for electrical purposes, as in the construction of induction coils, dynamo-electric machines, electric-light leads, and submarine telegraphs. Owing to its property of being readily deposited in a coherent metallic form from the solutions of its salts by electrolysis, copper is much used in the process of electrotyping, by means of which statues, bas-reliefs, and other works of art are reproduced. Copper, is, however, chiefly employed along with other metals in the form of alloys.

Alloys of copper.—The most important alloys of copper are those which it forms with zinc and with tin. The following is the composition of the principal zinc alloys of copper:

	Parts of copper.	Parts of zinc.
Brass (English), ...	2	1
Tombac,.	5	1
Muntz metal, ...	3	2

These alloys are all harder than copper. Brass is readily worked and does not clog the file like copper. Tombac is very ductile and malleable. *Dutch metal* is tombac beaten out into leaves $\frac{1}{52900}$ of an inch in thickness. Muntz metal is employed in the sheathing of ships, for which purpose it is rolled while hot into sheets. The color of these alloys is lighter the greater the proportion of zinc.

The following list contains the names and composition of the principal alloys of copper with tin:

	Parts of copper.	Parts of tin.
Speculum metal, ...	2	1
Bell metal, ...	4 to 5	1
Gun metal, ...	9	1

Speculum metal has a steel-gray color and takes a high polish. The quality of this alloy is said to be improved by the addition of a small quantity of arsenic, but this was denied by the late Lord Rosse. Bell metal has a yellowish-gray color and is very hard and sonorous. Gun metal is yellow and slightly malleable. All these alloys are brittle when cooled slowly, but acquire a certain degree of malleability when heated and then suddenly cooled by plunging into water.

Bronze is a copper-tin alloy of approximately the composition of gun metal, but with the addition of 2 or 3 per cent. of zinc. *Phosphor-bronze* is a valuable alloy obtained by fusing copper with phosphide of tin. It is exceedingly hard, tenacious, and elastic.

COMPOUND OF COPPER WITH HYDROGEN.

Cuprous hydride, $'\mathbf{Cu}'_2H_2$, is formed by the reducing action of a solution of hypophosphorous acid upon cupric sulphate. When the mixed solutions are heated to a temperature not higher than 70° C. (158° F.), the liquid assumes a green color and the hydride separates in the form of a yellow precipitate which becomes brown on standing. The liquid must be quickly cooled and the precipitate filtered off. Cuprous hydride is a very unstable compound, and is decomposed at 60° C. (140° F.) into hydrogen and metallic copper. It inflames spontaneously in chlorine. Hydrochloric acid dissolves it with evolution of hydrogen and formation of cuprous chloride.

COMPOUNDS OF COPPER WITH THE HALOGENS.

a. Cuprous Compounds.

Cuprous chloride, $'\mathbf{Cu}'_2Cl_2$.—*Molecular weight* = 197.4. *Molecular volume* ☐☐.—When finely divided copper or thin copper leaf is introduced into chlorine the metal ignites spontaneously, burning with a red light and yielding a mixture of cuprous and cupric chlorides. When copper is heated in a current of gaseous hydrocloric acid, cuprous chloride is formed and condenses in the colder parts of the tube. Cuprous chloride is further obtained by dissolving cuprous oxide in hydrochloric acid, or by reducing a solution of cupric chloride with stannous chloride. It may be readily prepared by boiling a solution of cupric chloride in hydrchloric acid with copper filings, with the addition of a few drops of a solution of platinic chloride, the precipitated platinum serving to establish a voltaic action with the copper. On pouring the filtered solution into water from which the air has been expelled by boiling, the cuprous chloride separates as a white crystalline powder consisting of microscopic tetrahedra. Cuprous chloride may also be obtained by slowly adding an intimate mixture of 2 parts of cupric oxide with 1 part of zinc dust to concentrated hydrochloric acid, until the liquid is saturated, and pouring the solution into water as above. Cuprous chloride may be obtained in distinct regular tetrahedra by crystallization

from a solution in hot concentrated hydrochloric acid. On exposure to air it absorbs oxygen and water, forming a cupric oxychloride. Exposure to sunlight with exclusion of air turns it violet if moist, but if dry it only acquires a faint yellow tinge. When heated it fuses, and on cooling solidifies to a crystalline mass; at a higher temperature it may be volatilized without decomposition. It is insoluble in water, but soluble in concentrated hydrochloric acid, in aqueous ammonia, and in sodic thiosulphate, yielding colorlorless solutions which possess the property of absorbing various gaseous hydrocarbons of the acetylene series (see Organic Chemistry), and also carbonic oxide, to form compounds. Thus with acetylene, $'''\mathbf{C}'_2\mathbf{H}_2$, it forms a dark-red powder which explodes on heating, and is believed to possess the composition $\left\{\begin{matrix} ''\mathbf{C}''_2{}'Cu'_2H \\ O \\ ''\mathbf{C}''_2{}'Cu'_2H \end{matrix}\right.$. When a solution of cuprous chloride in hydrochloric acid is saturated with carbonic oxide, it deposits nacreous scales of a compound probably of the formula $\mathbf{C}O(CuCl)_2,2\mathbf{O}H_2$. This compound is very unstable, readily evolving carbonic oxide, so that its composition has not been determined with certainty. The solution of cuprous chloride in ammonia deposits colorless rhombic dodecahedra of *cuprosammonic chloride* $\left\{\begin{matrix} \mathbf{N}H_3Cl \\ 'Cu'_2 \\ \mathbf{N}H_3Cl \end{matrix}\right.$. The same compound is obtained by heating copper turnings with a concentrated solution of ammonic chloride. The crystals undergo partial decomposition on exposure to the air. On heating they evolve ammonia. Cuprous chloride is also soluble in concentrated solutions of the alkaline chlorides, forming double compounds. The potassium compound crystallizes in octahedra of the formula $'\mathbf{Cu}'_2Cl_2,4KCl$.

Cuprous bromide, $'\mathbf{Cu}'_2Br_2$, is prepared like the chloride, which it closely resembles.

Cuprous iodide, $'\mathbf{Cu}'_2I_2$, is precipitated when potassic iodide is added to a solution of cupric sulphate, half the iodine being liberated:

$$\begin{array}{ccccccccc} 2\mathbf{S}O_2Cuo'' & + & 4KI & = & '\mathbf{Cu}'_2I_2 & + & 2\mathbf{S}O_2Ko_2 & + & I_2. \\ \text{Cupric sulphate.} & & \text{Potassic iodide.} & & \text{Cuprous iodide.} & & \text{Potassic sulphate.} & & \end{array}$$

The whole of the iodine is precipitated as cuprous iodide if a reducing agent, such as sulphurous acid or ferrous sulphate, is present:

$$\begin{array}{ccccccc} 2\mathbf{S}O_2Cuo'' & + & 2\mathbf{S}O_2Feo'' & + & 2KI & = & '\mathbf{Cu}'_2I_2 \\ \text{Cupric sulphate.} & & \text{Ferrous sulphate.} & & \text{Potassic iodide.} & & \text{Cuprous iodide.} \end{array}$$

$$\begin{array}{cccc} + & \left.\begin{matrix} \mathbf{S}O_2\text{—} \\ \mathbf{S}O_2\text{—} \\ \mathbf{S}O_2\text{—} \end{matrix}\right] ('Fe'''_2O_6)^{vi} & + & \mathbf{S}O_2Ko_2. \\ & \text{Ferric sulphate.} & & \text{Potassic sulphate.} \end{array}$$

Cuprous iodide is a grayish-white crystalline powder, insoluble in water and in dilute acids. It fuses at a red heat. It is the only known iodide of copper.

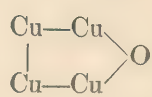
Cuprous fluoride, $'\mathbf{Cu}'_2F_2$, is prepared by treating cuprous hydrate with hydrofluoric acid. It forms a red fusible powder, insoluble in water, soluble in hydrochloric acid.

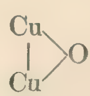
b. Cupric Compounds.

Cupric chloride, $\mathbf{Cu}Cl_2$, is prepared by dissolving copper in aqua-regia, or cupric oxide or carbonate in hydrochloric acid, and evaporating the solution. It crystallizes from water in green rhombic prisms with 2 aq.; these, when heated, part with their water of crystallization without losing hydrochloric acid, and yield the anhydrous compound. The concentrated aqueous solution is green, the dilute solution is blue. Cupric chloride is also soluble in alcohol. At a red heat it evolves chlorine and is converted into cuprous chloride.—Anhydrous cupric chloride absorbs gaseous ammonia, and is converted into a blue powder having the composition $\mathbf{Cu}Cl_2,6\mathbf{N}H_3$. An aqueous solution of the chloride, when saturated with ammonia, deposits dark-blue octahedra of a compound, $\mathbf{Cu}Cl_2,4\mathbf{N}H_3,\mathbf{O}H_2$. Both these compounds when heated to 150° C. are converted into *cuprammonic chloride*, $\left\{\begin{matrix}\mathbf{N}H_3Cl\\ Cu''\\ \mathbf{N}H_3Cl\end{matrix}\right.$, which forms a green powder.—Double compounds with the chlorides of potassium and ammonium, $\mathbf{Cu}Cl_2,2KCl,2\mathbf{O}H_2$, and $\mathbf{Cu}Cl_2,2\mathbf{N}H_4Cl,2\mathbf{O}H_2$, are obtained by allowing mixed solutions of the chlorides to crystallize.—When a solution of cupric chloride is digested with cupric hydrate, cupric *oxychlorides* of varying composition are obtained. A compound of this class having the formula $\left\{\begin{matrix}\mathbf{Cu}Cl\\ O\\ \mathbf{Cu}Ho\end{matrix}\right.,OH_2$ occurs native in Chili as the mineral *atacamite*, a green sand consisting of minute rhombic prisms. The pigment, *Brunswick green*, is a cupric oxychloride prepared by exposing to the air copper foil moistened with hydrochloric acid or ammonic chloride.

Cupric bromide, $\mathbf{Cu}Br_2$, is prepared like the chloride. It forms dark-colored crystals.
Cupric iodide is unknown.
Cupric fluoride, $\mathbf{Cu}F_2$, is prepared by treating the oxide with aqueous hydrofluoric acid. It crystallizes from water in small blue crystals with 2 aq.

COMPOUNDS OF COPPER WITH OXYGEN AND HYDROXYL.

Cuprous quadrantoxide, . $\left\{\begin{matrix}\mathbf{Cu}\\ Cu\\ Cu\\ \mathbf{Cu}\end{matrix}\right\}O$ 

Cuprous oxide, ... $\left\{\begin{matrix}\mathbf{Cu}\\ \mathbf{Cu}\end{matrix}\right.O$ 

Cupric oxide, ... $\mathbf{Cu}O$ $\mathbf{Cu}{=}O$

$$\text{Cuprous hydrate, . . } 4'\mathbf{Cu}'_2O,\mathbf{O}H_2, \text{ or } \begin{array}{l} \left\{\begin{array}{l} \mathbf{Cu}Ho \\ \mathbf{Cu} \end{array}\right. \\ \left\{\begin{array}{l} \mathbf{Cu} \\ \mathbf{Cu} \end{array}\right. O \\ \left\{\begin{array}{l} \mathbf{Cu} \\ \mathbf{Cu} \end{array}\right. O \\ \left\{\begin{array}{l} \mathbf{Cu} \\ \mathbf{Cu}Ho \end{array}\right. O \end{array}$$

$$\begin{array}{c} O—Cu—Cu—O—Cu—Cu—O—Cu—Cu—O—Cu—Cu—O \\ \begin{array}{lcr} | & \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad & | \\ H & & H \end{array} \end{array}$$

$$\text{Cupric hydrate, ... } \mathbf{Cu}Ho_2 \qquad Cu<\begin{array}{l} O—H \\ O—H \end{array}$$

Cuprous quadrantoxide, Cu_4O, is obtained in a hydrated condition as a very unstable green powder by adding a solution of cupric sulphate to a dilute solution of stannous chloride in caustic potash.

Cuprous oxide, $'\mathbf{Cu}'_2O$, occurs native as *red copper-ore*, forming red octahedra belonging to the regular system, but is more frequently found massive. When copper is superficially oxidized by heating in air, the outer portions of oxide consist of cupric oxide, but the inner portions, which are adjacent to the unaltered metal, have a composition approximating more closely to that of cuprous oxide. When a mixture of cuprous chloride with anhydrous sodic carbonate is heated in a closed crucible and the mass is lixiviated with water, cuprous oxide remains as a red powder. The precipitate of cupric hydrate produced by caustic alkalies in a solution of cupric sulphate redissolves on the addition of grape sugar, yielding a blue solution, which when gently heated deposits cuprous oxide as a red crystalline precipitate consisting of minute octahedra. The reduction is effected at the expense of the grape sugar, which undergoes oxidation. Thus prepared, cuprous oxide undergoes no change when exposed to the air at ordinary temperatures, but when heated in air is converted into cupric oxide. With exclusion of air it may be fused at a red heat. It is insoluble in water, but soluble in aqueous ammonia, yielding a colorless liquid, which rapidly absorbs oxygen from the air and becomes blue. Hydrochloric acid converts it into colorless cuprous chloride, soluble in an excess of the acid. With most of the oxy-acids it does not yield cuprous salts: in some cases one-half of the copper present in the oxide dissolves to form a cupric salt, the other half remaining behind as metallic copper; in other cases the whole of the oxide dissolves, yielding a cupric salt, the cuprous oxide undergoing oxidation at the expense of a portion of the acid. Thus with dilute sulphuric acid the reaction takes place according to the first of these modes:

$$\underset{\text{Cuprous oxide.}}{'\mathbf{Cu}'_2O} + \underset{\text{Sulphuric acid}}{\mathbf{S}O_2Ho_2} = \underset{\text{Cupric sulphate.}}{\mathbf{S}O_2Cuo''} + Cu + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

With hot concentrated sulphuric acid, on the other hand, the second reaction occurs:

$$'Cu'_2O + 3SO_2Ho_2 = 2SO_2Cuo'' + SO_2 + 3OH_2.$$

Cuprous oxide.	Sulphuric acid.	Cupric sulphate.	Sulphurous anhydride.	Water.

Nitric acid dissolves the whole as cupric nitrate with evolution of nitric oxide.

CUPRIC OXIDE, **CuO**.—This oxide occurs sparingly in nature as the mineral *tenorite.* It is obtained by igniting metallic copper in air, or by igniting cupric nitrate. It forms black scales or powder, according to the mode of preparation. When strongly ignited it cakes together, and at a white heat fuses, parting with a portion of its oxygen and being converted into an oxide of the formula Cu_5O_3. When heated to redness with carbon, or in a current of carbonic oxide or hydrogen, it is reduced to the metallic state. In a similar manner, when organic substances containing carbon and hydrogen are heated with it, these two constituents are oxidized to carbonic anhydride and water, for which reason it is employed in the ultimate analysis of organic compounds. It is also used to impart a green color to glass. It dissolves in acids, yielding the cupric salts.

Cuprous hydrate, $4'Cu'_2O,OH_2$, is obtained as a bright yellow precipitate when a solution of cuprous chloride in hydrochloric acid is poured into an excess of cold caustic alkali. It retains its water of hydration at 100° C. (212° F.), but parts with it completely at 360° C. (680° F.). It is soluble in ammonia and hydrochloric acid, yielding the same compounds as cuprous oxide. When exposed to the air it undergoes oxidation and becomes blue.

CUPRIC HYDRATE, $CuHo_2$, is obtained as a pale blue bulky precipitate when an excess of caustic potash or soda is added to the solution of a cupric salt in the cold. It is insoluble in excess of the precipitant except in presence of certain organic substances, such as sugar and tartaric acid. When the precipitate is heated with the alkaline liquid it blackens, and is partially converted into cupric oxide; but after washing and drying at ordinary temperatures it may be heated to 100° C. (212° F.) without giving off water. Cuprous hydrate is soluble in aqueous ammonia, yielding a blue solution, which possesses the remarkable property of dissolving cellulose in its various forms—cotton, linen, paper, etc. The cellulose is precipitated in the amorphous state by acids, salt, sugar, and various other substances.

OXY-SALTS OF COPPER.

CUPRIC NITRATE, $\begin{matrix}NO_2\\NO_2\end{matrix}Cuo'',3OH_2$.—The solution of copper or cupric oxide in nitric acid yields on evaporation blue prismatic crystals of the above composition. These are deliquescent and soluble in alcohol. The anhydrous salt has not been prepared, as the aquate, when heated to about 65° C. (149° F.), parts with nitric acid and water, yielding a green basic salt of the formula $NOHo(OCuHo)_2$. Owing to the readiness with which cupric nitrate is decomposed with liberation of nitric acid, this salt possesses oxidizing properties. Moist

crystals of the nitrate, wrapped up in tinfoil, act violently upon it, oxidizing it to stannic oxide, frequently with emission of sparks. On evaporating mixed solutions of cupric nitrate and ammonic nitrate over a flame, when a certain concentration is attained the whole liquid suddenly deflagrates like loose gunpowder, evolving a dense brown cloud of finely divided cupric oxide. Cupric nitrate is employed in dyeing and calico-printing in some cases in which an oxidizing agent is required to produce the color on the fibre.—A concentrated solution of cupric nitrate in ammonia deposits dark blue rhombic crystals of a compound—

$$\begin{matrix}NO_2\\NO_2\end{matrix}Cuo'',4NH_3 = \left.\begin{matrix}NOHo(NH_2)(NH_3O\\NOHo(NH_2)(NH_3O\end{matrix}Cu''\right)''.$$

Cupric carbonates.—The normal carbonate is unknown. Various basic carbonates occur in nature. *Mysorin* is dicupric carbonate, $CCuo''_2$. *Malachite* is dicupric carbonate dihydrate, $CO(OCu''Ho)_2$. It forms monoclinic crystals of a brilliant green color, more frequently botryoidal masses, with a structure which is generally fibrous. The massive variety takes a high polish, and is employed for ornamental purposes. The same compound is formed as a green rust by the joint action of water and air upon copper, and is then known as *verdigris*. *Blue malachite* or *azurite* is a dihydric tricupric dicarbonate, $\left\{\begin{matrix}CHoCuo''\\Cuo''\\CHoCuo''\end{matrix}\right.$. It occurs in dark-blue monoclinic crystals.

Cupric sulphate (*Dihydric cupric sulphate*), $SOHo_2Cuo'',4OH_2$.—This salt, also known as *blue vitriol*, is obtained on a large scale by roasting copper pyrites and lixiviating the mass with water. The iron chiefly remains behind as oxide, whilst the cupric sulphate dissolves, and on evaporation is deposited in crystals of the above formula. The first crystallization is relatively pure; the crystals from the mother liquor contain iron (as ferrous sulphate), from which they can best be freed by recrystallization with the addition of nitric acid. Ferrous sulphate is capable of crystallizing with cupric sulphate in varying proportions (see below), and the two substances cannot be completely separated by crystallization. The addition of nitric acid converts the ferrous sulphate into a ferric salt, which does not possess this property.—Cupric sulphate is thus obtained in large blue triclinic crystals, soluble in $2\frac{1}{2}$ parts of water at ordinary temperatures, in $\frac{1}{2}$ part at 100° C. (212° F.). The crystals effloresce in dry air, and part with the four molecules of water of crystallization at 100° C. (212° F.), leaving the salt $SOHo_2Cuo''$, which at a temperature above 200° C. (392° F.) is converted into anhydrous cupric sulphate, SO_2Cuo'', a colorless salt which rapidly attracts moisture and becomes of a blue color.—Various basic sulphates of copper are known. By heating the normal sulphate to redness for several hours, *dicupric sulphate*, $SOCuo''_2$, is obtained as an orange-yellow powder. Cold water converts this salt into ordinary cupric sulphate, which dissolves, and an insoluble green basic sulphate of the formula $SHo_2(OCu''Ho)_4$, *dihydric tetracupric sulphate dihydrate*, a substance which occurs native as the mineral *brochantite*. With boiling water the

orange-yellow powder yields another basic sulphate—*hydric tricupric sulphate trihydrate*, $\mathbf{S}O\text{Ho}(OCu''\text{Ho})_3$.—A concentrated solution of cupric sulphate in ammonia deposits, especially on the addition of alcohol, dark-blue rhombic crystals of the compound $\mathbf{S}O_2\text{Cuo}'',4\mathbf{N}H_3,\mathbf{O}H_2$ $=\mathbf{S}\text{Ho}_2(NH_2)_2\left\{\begin{matrix}NH_3O\\Cu''\\NH_3O\end{matrix}\right)'',\mathbf{O}H_2$, which on heating to 150° C. (302° F.) is converted into a green powder, consisting of *cuprammonic sulphate*, $\mathbf{S}O_2\left\{\begin{matrix}NH_3O\\Cu''\\NH_3O\end{matrix}\right)''$. Anhydrous cupric sulphate absorbs gaseous ammonia with great avidity, yielding the compound $\mathbf{S}O_2\text{Cuo}'',5\mathbf{N}H_3$.—Cupric sulphate forms with the alkaline sulphates double salts crystallizing in monoclinic forms, and isomorphous with the corresponding double salts of the alkalies with zinc and magnesium. Thus with potassic sulphate it forms *dipotassic cupric disulphate*, $\left\{\begin{matrix}\mathbf{S}O_2\text{Ko}\\\text{Cuo}''\\\mathbf{S}O_2\text{Ko}\end{matrix}\right.,6\mathbf{O}H_2$.—From mixed solutions of cupric sulphate with one of the sulphates of the dyad metals, magnesium, zinc, nickel, and iron (ferrous), crystals are deposited, consisting of isomorphous mixtures of the two sulphates present. If cupric sulphate predominates in the solution, the mixed crystals are triclinic like those of cupric sulphate, and like the latter salt contain 5 aq. (including the molecule of water of constitution); if the other sulphate predominates, the mixed crystals assume the form of this sulphate, rhombic or monoclinic, and, like the rhombic and monoclinic sulphates of this isomorphous group, contain 7 aq. (including the molecule of water of constitution).—Cupric sulphate is employed in the preparation of pigments containing copper, in calico-printing, and in electrotyping.

Cupric phosphates.—The normal phosphate, $\left\{\begin{matrix}\mathbf{P}O\text{Cuo}''\\\text{Cuo}''\\\mathbf{P}O\text{Cuo}''\end{matrix}\right.,3\mathbf{O}H_2$, is most readily prepared pure by digesting cupric carbonate with dilute phosphoric acid and heating to 70° C. (158° F.) the blue solution thus obtained. The salt separates as a bluish-green powder, insoluble in water, soluble in acids and in ammonia. It is also formed when hydric disodic phosphate is added to an excess of a solution of a normal cupric salt. If, on the other hand, the solution of the cupric salt be added to an excess of the alkaline phosphate, a precipitate is obtained similar in appearance, but consisting of *hydric cupric phosphate*, $\mathbf{P}O\text{HoCuo}''$. When the normal phosphate is heated with water in sealed tubes, it is decomposed into free phosphoric acid and a basic salt—*dicupric phosphate hydrate*, $\mathbf{P}O\text{Cuo}''(OCu''\text{Ho})$—which also occurs in nature as the mineral *libethenite*, and crystallizes in dark olive-green rhombic prisms. Another native basic cupric phosphate is the mineral *phosphochalcite*, $\mathbf{P}O(OCu\text{Ho})_3$, *tricupric phosphate trihydrate*, which forms green monoclinic crystals or botryoidal masses.

Cupric arsenates.—The normal arsenate, $\left\{\begin{matrix}\mathbf{As}O\text{Cuo}''\\\text{Cuo}''\\\mathbf{As}O\text{Cuo}''\end{matrix}\right.,2\mathbf{O}H_2$, is obtained by heating together cupric nitrate and calcic arsenate. It forms a blue amorphous powder. Basic arsenates also occur as minerals, and correspond closely to the basic phosphates, with which they are isomorphous. *Olivenite* is a *dicupric arsenate hydrate*, $\mathbf{As}O\text{Cuo}''(OCu''\text{Ho})$.

Cupric arsenite.—*Hydric cupric arsenite*, $\mathbf{As}\text{HoCuo}''$, a compound employed as a pigment under the name of *Scheele's green*, is prepared by adding to the solution of a cupric salt a solution of arsenious anhydride, and then carefully neutralizing with ammonia or caustic soda. It is of a light green color. It is insoluble in water, but readily soluble in caustic potash, yielding a blue liquid. The solution gradually deposits cuprous oxide.

Cupric silicates.—Two of these occur in nature. *Dioptase*, a *hydric cupric silicate hydrate*, $\mathbf{Si}OHo(OCu''Ho)$, forms emerald-green hexagonal crystals. *Chrysocolla* is a *trihydric cupric silicate hydrate*, $\mathbf{Si}Ho_3(OCu''Ho)$. It forms green botryoidal masses.

COMPOUNDS OF COPPER WITH SULPHUR.

Cuprous sulphide, ...	$\left\{\begin{matrix}\mathbf{Cu}\\ \mathbf{Cu}\end{matrix}\right. S''$.	$\begin{matrix}Cu\\ \vert\\ Cu\end{matrix}\!>\!S$
Cupric sulphide, ...	$\mathbf{Cu}S''$.	$Cu{=}S$

CUPROUS SULPHIDE, $'\mathbf{Cu}'_2S$.—This compound occurs native as *copper glance*, and forms lead-gray rhombic tables or prisms with a metallic lustre, and having a sp. gr. of 5.5 to 5.8. The same compound is obtained as a black, brittle mass by heating together 4 parts of copper filings and 1 part of sulphur, or by burning copper in sulphur vapor.

CUPRIC SULPHIDE, $\mathbf{Cu}S$, also occurs native as the mineral *indigo-copper*, but much less abundantly than the cuprous compound. It sometimes forms dark-blue hexagonal crystals with a semi-metallic lustre, but more frequently occurs massive. Its sp. gr. is 4.6. It may be obtained as a blue powder by heating finely divided copper with flowers of sulphur, avoiding a temperature higher than the boiling point of sulphur. It is obtained as a black amorphous precipitate when sulphuretted hydrogen is passed into solutions of cupric salts, and in this condition is readily oxidized if exposed to the air while still moist. The precipitated sulphide is insoluble in potassic and sodic sulphides, somewhat soluble in yellow ammonic sulphide; readily soluble in potassic cyanide and in hot nitric acid. When cupric sulphide is heated with exclusion of air, or in a current of hydrogen, it parts with half its sulphur and is converted into cuprous sulphide.—When an ammoniacal solution of a copper salt is precipitated with sulphuretted hydrogen a black precipitate of cupric sulphide is obtained. If this precipitate be washed for a very long time with sulphuretted hydrogen water, until the last traces of ammonia compounds are removed, the black sulphide at last goes into solution, yielding a dark-brown liquid which is believed by some chemists to contain a *colloidal* modification of the sulphide. Solutions of salts precipitate from the liquid insoluble cupric sulphide. On evaporation the black liquid dries up to a black lustrous film. Similar colloidal modifications of sulphides have been obtained in the case of various other heavy metals.*

* It is, however, probable that these so-called colloidal sulphides are nothing more than ordinary sulphides in a state of very fine subdivision. Ebell, who has advanced this view, has shown that the finest ultramarine, obtained by grinding and levigation, can be removed by filtration from liquids containing a salt in solution; but if the ultramarine upon the filter be washed with pure water, it passes through the filter as soon as the salt solution has been sufficiently removed, and yields a blue liquid which to the eye is perfectly transparent, but which under the microscope is seen to contain minute suspended particles of ultramarine. In pure water these minute particles show no tendency to subside; but the addition of a small quantity of the solution of a salt precipitates the ultramarine. If the salt solution be added to a drop of the blue liquid

COMPOUNDS OF COPPER WITH NITROGEN, PHOSPHORUS, AND ARSENIC.

Cuprous nitride, $\mathbf{N}_2('Cu'_2)''_3$, is obtained as a dark green powder when gaseous ammonia is passed over finely-divided cupric oxide heated to 250° C.:

$$\underset{\text{Cupric oxide.}}{6\mathbf{Cu}O} + \underset{\text{Ammonia.}}{4\mathbf{N}H_3} = \underset{\text{Cuprous nitride.}}{\mathbf{N}_2('Cu'_2)''_3} + N_2 + \underset{\text{Water.}}{6\mathbf{O}H_2}.$$

At 300° C., it is decomposed, with a slight explosion, into its elements.

Cuprous phosphide, $\mathbf{P}_2('Cu'_2)''_3$, is formed when cuprous chloride is heated in a current of phosphoretted hydrogen, or when the vapor of phosphorus is passed over copper foil heated to low redness. By fusing the compound under a layer of borax it may be obtained in the form of a silver-white regulus of sp. gr. 6.59, very brittle, and capable of taking a polish. Hydrochloric acid is almost without action upon it, but nitric acid dissolves it readily.

Cupric phosphide, $\mathbf{P}_2Cu''_3$, is prepared in a similar manner by passing phosphoretted hydrogen over heated cupric chloride. It forms a black lustrous powder, which when heated in a current of hydrogen is converted into cuprous phosphide. It is also formed as a black precipitate when phosphoretted hydrogen is passed into the solution of a cupric salt (p. 342).

Cuprous arsenide, $\mathbf{As}_2('Cu'_2)''_3$, occurs in Chili as the mineral *domeykite*, forming tin-white or silver-white masses. Other arsenides of copper also occur as minerals.

General Properties and Reactions of the Compounds of Copper.—The soluble compounds of copper have a disagreeable metallic taste, and are poisonous, causing vomiting and death.

a. *Cuprous Compounds.*—The cuprous salts are colorless. They are generally insoluble in water, but soluble in hydrochloric acid and ammonia. In solution they rapidly absorb oxygen from the air, and are converted into cupric salts. *Caustic alkalies* precipitate yellow cuprous hydrate, which is converted on boiling into red cuprous oxide.

b. *Cupric Compounds.*—The cupric salts are white in the anhydrous state, blue or green when hydrated. They are nearly all soluble. The solutions redden blue litmus. *Caustic alkalies* precipitate blue *cupric hydrate*, which on boiling is partially converted into cupric oxide and becomes black. The presence of sugar, tartaric acid, and various other organic substances, renders the cupric hydrate soluble in an excess of alkali. *Ammonia* gives a similar precipitate, which is, however, soluble in excess, yielding a deep-blue liquid. *Sulphuretted hydrogen* precipitates from acid solutions brownish-black cupric sulphide, slightly soluble in yellow ammonic sulphide, readily soluble in potassic cyanide, and in hot nitric acid. *Potassic ferrocyanide* gives a brown precipitate, insoluble in hydrochloric acid.

From solutions of copper compounds *zinc* and *iron* precipitate metallic copper. All compounds of copper, when heated with sodic carbonate on charcoal in the reducing flame of the blowpipe, yield a bead of metallic copper. A borax bead containing a copper salt, and heated

under the microscope, the separate particles of ultramarine are seen to unite into aggregations, each consisting of a number of particles. On evaporation, the blue liquid yields a lustrous blue film adhering to the sides of the vessel.

The behavior of this finely-divided ultramarine—a substance which cannot in any sense be regarded as *colloidal*—corresponds therefore, in all the above particulars, with that of the metallic sulphides referred to.

in the oxidizing flame, is green while hot and blue when cold; in the reducing flame the bead is colorless if the proportion of copper be small, but, if the proportion of copper be large, the bead is red from the presence of reduced copper. The compounds of copper color the non-luminous flame green or blue. Cupric chloride gives a banded flame-spectrum, this being the spectrum of the compound. The spark-spectrum of copper contains a number of lines, among which some of those in the green are especially prominent.

CHAPTER XXXV.

TRIAD ELEMENTS.

SECTION II.

GOLD, Au_2?

Atomic weight = 196. *Probable molecular weight* = 392. *Sp. gr.* 19.3 to 19.5. *Fuses at* 1240° C. (2264° F.). *Atomicity* ′ *and* ‴. *Evidence of atomicity:*

Aurous chloride, ...	$AuCl$.
Aurous iodide, ...	AuI.
Auric chloride, ...	$Au'''Cl_3$
Auric hydrate, ...	$Au'''Ho_3$.

History.—Gold has been known and prized from the earliest historical times.

Occurrence.—Gold occurs widely distributed, but mostly only in small quantity. It is almost always found in the native state, sometimes in crystals, sometimes in dendritic forms produced by the regular aggregation of crystals, but most frequently in irregular masses termed *nuggets.* In matrix it is found disseminated throughout quartz veins or reefs. The alluvial deposits produced by the disintegration of the auriferous rocks form the chief sources of the metal. The principal gold-fields are those of California and Australia. Gold is still extracted from the sand of rivers in Hungary and Transylvania, but the importance of these sources has diminished since the discovery of the Australian and Californian fields. Native gold generally contains more or less silver; if the percentage of silver exceeds 36 per cent. this native alloy is termed *electrum.* Gold is found in combination with bismuth and tellurium in a few rare minerals, and alloyed with mercury as an amalgam. Traces of the metal occur in many ores of silver, copper, and lead, and in iron pyrites. In spite of the smallness of the quantity present, it is possible in some of these cases to extract the gold with profit (see p. 450).

Extraction.—Native gold is mechanically separated from the alluvial deposits with which it is mixed by washing away the lighter earthy particles—either by the simple manual processes of *pan-washing* or *cradle-washing*, or, on a large scale, by *hydraulic gold-mining*. In the latter process enormous jets of water are employed to remove the whole of the alluvial deposit down to the bed-rock. The stream of water, carrying with it the disintegrated deposit, flows through a long sloping tunnel bored in the rock. Along the bottom of the tunnel are placed "sluice-boxes" containing a small quantity of mercury. The particles of gold fall into the sluice-boxes and are arrested by the mercury with which they form an amalgam. The tunnel is cleared at intervals of from ten to twenty days: the amalgam of gold is removed, and the mercury expelled by distillation. In *quartz-mining* the auriferous quartz is stamped to a fine powder by special machinery, and the gold extracted by amalgamation.

Refining.—One of the simplest and most efficient refining processes is that devised by F. B. Miller. The gold, which must not contain more than 10 per cent of silver, is melted in a clay crucible glazed inside with borax, and a current of chlorine is passed through the molten metal. The silver is thus converted into argentic chloride, which rises to the surface and is prevented from volatilizing by a layer of fused borax; other foreign metals, such as zinc, antimony, bismuth, and tin, are volatilized as chlorides. The metal thus purified contains from 99.1 to 99.7 per cent. of gold.

Pure gold may be prepared by dissolving the metal in aqua-regia, and, after expelling the excess of nitric acid, precipitating the gold by some reducing agent, such as ferrous sulphate. The finely divided gold is obtained in a coherent form by fusion with a mixture of borax and nitre.

Properties.—Gold is a lustrous metal, of a yellow color when the light is only once reflected, but red when the light is several times reflected from the surface of the metal before reaching the eye (p. 400). It is the most malleable and ductile of the metals (pp. 409 and 410). Very thin gold leaf transmits green light. When pure it is nearly as soft as lead. It fuses at 1240° C. (2264° F.), the molten metal emitting a bluish-green light. At very high temperatures it is volatile. It is quite unalterable in air, oxygen, and steam, at all temperatures. No single acid, with the exception of selenic, has any action upon it; but aqua-regia, and all other liquids containing or evolving chlorine, dissolve it with formation of auric chloride ($\mathbf{Au}Cl_3$). It combines with chlorine and bromine at ordinary temperatures, and with phosphorus when heated in its vapor. It is precipitated from its solutions by most other metals, and by most reducing agents. Ferrous sulphate precipitates it as a brown powder without metallic lustre; oxalic acid, in glistening yellow scales.

Uses.—Gold is employed for coinage, for ornaments, and in gilding. Non-metallic surfaces are gilt with gold-leaf. Metals are gilt by electrodeposition, employing a solution of auric chloride in potassic cyanide (the solution contains auric potassic cyanide, $\mathbf{Au}Cy_3,KCy$) and using a gold plate as positive electrode.

Alloys.—Pure gold is employed in the preparation of gold-leaf and of the solutions for electro-gilding, but owing to its softness is not suited for the manufacture of objects which have to resist the wear of ordinary use. For jewellery or coinage gold is therefore alloyed with copper, or with silver, or with both, these admixtures imparting to the gold the requisite hardness. The copper alloy has a reddish tinge, that with silver is whiter than pure gold.

The proportion of gold in an alloy is frequently expressed in *carats*, or parts per 24: thus 24-carat gold is pure gold, 22-carat gold contains 22 parts of gold in 24 parts of the alloy, and so on. In most countries the composition of various standard alloys for jewellery and coinage is fixed by law. In England there are five legal standards: 22-carat—the standard gold employed for coinage, the two remaining parts in this case consisting of copper—18, 15, 12 and 9-carat gold. In the case of coinage standards, however, it is more usual to express the proportion of gold in parts per mille of the alloy, this expression being known as the *fineness* of the alloy. The English 22-carat standard gold has thus a fineness of 916.66. Most other European countries employ a coinage standard having a fineness of 900.

Gold forms two classes of compounds, *aurous* and *auric*. In the first of these it is a monad, in the second a triad.

COMPOUNDS OF GOLD WITH THE HALOGENS.

a. Aurous Compounds.

Aurous chloride, AuCl, is obtained by heating auric chloride, $AuCl_3$, to 185° C. (365° F.). It is a yellowish-white powder, which is decomposed at a higher temperature into gold and chlorine. Water decomposes it into metallic gold and the trichloride.

Aurous iodide, AuI, is formed by the action of hydriodic acid upon auric oxide:

$$\underset{\text{Auric oxide.}}{Au_2O_3} + \underset{\text{Hydriodic acid.}}{6HI} = \underset{\text{Aurous iodide.}}{2AuI} + \underset{\text{Water.}}{3OH_2} + 2I_2,$$

and in all similar cases when the formation of an auric iodide might be expected, the latter compound undergoing decomposition into $AuI + I_2$—thus by the action of potassic iodide upon auric chloride:

$$\underset{\text{Auric chloride.}}{AuCl_3} + \underset{\text{Potassic iodide.}}{3KI} = \underset{\text{Aurous iodide.}}{AuI} + I_2 + \underset{\text{Potassic chloride.}}{3KCl.}$$

—Aurous iodide forms a lemon-yellow powder, which is decomposed, slowly at ordinary temperatures, rapidly on heating, into its elements.

b. Auric Compounds.

AURIC CHLORIDE, $AuCl_3$.—This compound is obtained by the action of chlorine upon gold, or by dissolving gold in aqua-regia, evaporating to dryness, taking up with water, evaporating again to dryness, and heating carefully to 150° C. (302° F.). The anhydrous chloride forms a brown crystalline deliquescent mass. Though decomposed at 185° C. (365° F.), as already mentioned, into aurous chloride and chlorine, it may be sublimed in a current of chlorine at 300° C. (572° F.), and is thus obtained in long red needles. When a hot concentrated aqueous

solution of auric chloride is allowed to cool, an aquate of the formula $\mathbf{Au}Cl_3,2\mathbf{O}H_2$, is deposited in large orange-colored crystals.

Auric chloride forms numerous compounds with other metallic chlorides and with hydrochloric acid. The hydrochloric acid compound, sometimes called *hydrauric acid*, has the formula $\mathbf{Au}Cl_3,HCl,3\mathbf{O}H_2$, and crystallizes from the concentrated solution of gold in aqua-regia in long yellow needles. *Auric potassic chloride* forms two aquates—$(\mathbf{Au}Cl_3,KCl)_2,\mathbf{O}H_2$, crystallizing in needles, and $\mathbf{Au}Cl_3,HCl,2\mathbf{O}H_2$, crystallizing in large rhombic tables. *Auric sodic chloride*, $\mathbf{Au}Cl_3,NaCl,2\mathbf{O}H_2$, crystallizes in yellowish-red prisms. *Auric ammonic chloride* forms light yellow rhombic tables, $(\mathbf{Au}Cl_3,\mathbf{N}H_4Cl)_2 5\mathbf{O}H_2$, or monoclinic plates $(\mathbf{Au}Cl_3,NH_4Cl)5\mathbf{O}_4H_2$. These double chlorides are sometimes referred to as *chloraurates*, thus *potassic chloraurate*.

Auric bromide, $\mathbf{Au}Br_3$, forms a black crystalline mass.

Auric iodide, $\mathbf{Au}I_3$, is not known as such, but several double compounds of this iodide with iodides of other metals have been prepared.

COMPOUNDS OF GOLD WITH OXYGEN AND HYDROXYL.

Aurous oxide, ... $\mathbf{O}Au_2$. Au—O—Au.

$$\text{Auric oxide } (\textit{Auric anhydride}) \left\{ \begin{array}{l} \mathbf{Au}O \\ O \\ \mathbf{Au}O \end{array} \right. . \quad O{=}Au{-}O{-}Au{=}O.$$

$$\text{Auric hydrate, } \ldots\ldots \quad \mathbf{Au}Ho_3. \quad Au \begin{array}{l} \diagup O{-}H \\ {-}O{-}H. \\ \diagdown O{-}H \end{array}$$

Aurous oxide, $\mathbf{O}Au_2$, is obtained as a violet-black powder by the action of dilute caustic potash upon aurous chloride. At 150° C. (302° F.) it is decomposed into its elements. With hydrochloric acid it yields auric chloride and metallic gold:

$$\underset{\text{Aurous oxide.}}{3\mathbf{O}Au_2} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Auric chloride.}}{2\mathbf{Au}Cl_3} + 2Au_2 + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

Sulphuric and nitric acids are without action upon it, but aqua-regia dissolves it readily.

Auric oxide (*Auric anhydride*), $\mathbf{Au}_2O_3$.—This compound is prepared by heating a solution of auric chloride with magnesia and treating the precipitate, which consists of *magnesic aurate*,

$$\begin{array}{l}\mathbf{Au}O \\ \mathbf{Au}O\end{array} Mgo'',$$

with concentrated nitric acid, in which the whole dissolves. Water precipitates *auric hydrate*, $\mathbf{Au}Ho_3$, as a reddish-yellow powder, which by gentle heating is converted into the oxide. It forms a brown powder which is partially decomposed at 100° C. (212° F.), wholly at 245° C. (473° F.), into its elements. It is the anhydride of *auric acid*, $\mathbf{Au}OHo$, and dissolves in dilute caustic potash to form *potassic aurate*, which crystallizes in light yellow needles of the formula $\mathbf{Au}OKo,3\mathbf{O}H_2$.

—A derivative of auric anhydride is *fulminating gold*, a compound which is formed by the union of four molecules of ammonia with one of auric anhydride, and which may be regarded as possessing the constitution $\left\{\begin{array}{l} \mathbf{Au}(NH_2)(NH_4O) \\ O \\ \mathbf{Au}(NH_2)(NH_4O) \end{array}\right.$. It is best prepared by treating auric hydrate with aqueous ammonia. It forms a yellowish-brown or greenish-yellow powder, which when dry explodes with great violence by heat or percussion. A similar compound, which however appears to contain chlorine, separates when ammonia is added to a solution of auric chloride.

Auric hydrate, $\mathbf{Au}Ho_3$, may be obtained either as above described, or by electrolyzing dilute sulphuric acid, employing a gold plate as positive electrode, when the hydrate is formed as a yellow crust on the electrode.

OYY-SALTS OF GOLD.

Simple oxy-salts of gold are not known. Double salts have however been prepared, such as the double thiosulphate of gold and sodium, $\mathbf{S}O_2AuoAus,3\mathbf{S}O_2NaoNas,4\mathbf{O}H_2$, which might also be formulated—

$$\left\{\begin{array}{l} \mathbf{S}Ho_2NaoAus \\ O \\ \mathbf{S}Ho_2NaoNas \\ O \\ \mathbf{S}Ho_2NaoNas \\ O \\ \mathbf{S}Ho_2NaoAus \end{array}\right] O, \quad \textit{octohydric diaurous hexasodic tetrathiosulphate.}$$

It is formed when a dilute neutral solution of auric chloride is added to an excess of a solution of sodic thiosulphate. A reduction of the gold from the auric to the aurous condition occurs, the red liquid which is at first formed becoming colorless. The salt is then precipitated by the addition of strong alcohol. It crystallizes in colorless needles which have a sweet taste. Neither the gold nor the thiosulphuric acid can be detected by the usual tests: the gold is not precipitated by reducing agents, and no separation of sulphur occurs on the addition of dilute acids.

Double sulphites of gold with the alkali metals are also known. *Aurous ammonic sulphite* has the formula

$$\mathbf{S}OAmo_2,3\mathbf{S}OAuoAmo,3\mathbf{O}H_2.$$

Purple of Cassius.—This remarkable compound is obtained as a flocculent purple precipitate when a very dilute mixed solution of stannous and stannic chloride is gradually added to a dilute neutral solution of auric chloride. It contains one or both of the oxides of tin. Its nature is not known with certainty, but it is supposed to be a hydrated *stannous diaurous distannate*,

$$\mathbf{Sn}_2O_2Sno''Auo_2,4\mathbf{O}H_2.$$

Its composition, however, is apt to vary with the mode of preparation. The compound is decomposed by acids with separation of metallic gold. It is insoluble in solutions of caustic potash and caustic soda, but soluble in ammonia, yielding a deep purple liquid which is bleached by exposure to light with deposition of metallic gold and formation of ammonic stannate. Purple of Cassius is employed to impart a magnificent red color to glass. The color depends upon the presence in the glass of metallic gold in a state of minute subdivision.

COMPOUND OF GOLD WITH SULPHUR.

Diaurous disulphide, $'\mathbf{S}'_2Au_2$, is precipitated by sulphuretted hydrogen from cold solutions of auric chloride:

$2\mathbf{Au}Cl_3$	+	$3\mathbf{S}H_2$	=	$'\mathbf{S}'_2Au_2$	+	$6HCl$	+	S.
Auric chloride.		Sulphuretted hydrogen.		Diaurous disulphide.		Hydrochloric acid.		

It forms a black precipitate, insoluble in water, soluble in solutions of the alkaline sulphides, with formation of double sulphides such as $\mathbf{S}NaAu$:

$'\mathbf{S}'_2Au_2$	+	$2\mathbf{S}Na_2$	=	$2\mathbf{S}NaAu$	+	$'\mathbf{S}'_2Na_2$.
Diaurous disulphide.		Disodic sulphide.		Sodic aurous sulphide.		Disodic disulphide.

From hot solutions of gold salts sulphuretted hydrogen precipitates metallic gold.

General Properties and Reactions of the Compounds of Gold.—Gold is precipitated from its solutions by most reducing agents —*e.g.*, *ferrous sulphate, mercurous nitrate, oxalic acid, formic acid, sulphurous acid*—as finely divided metallic gold. A mixture of *stannous and stannic chlorides* produces a characteristic precipitate of purple of Cassius (p. 555). All gold compounds are converted into metallic gold when ignited with exposure to air. The compounds of gold do not color the non-luminous flame.

Section III.

THALLIUM, Tl_2?

Atomic weight = 204. *Probable molecular weight* = 408. *Sp. gr* 11.8 *to* 11.9. *Fuses at* 294° C. (561.2° F.). *Atomicity* ′ *and* ‴. *Evidence of atomicity:*

Thallous chloride, ...	$TlCl$.
Thallous oxide, ...	$\mathbf{O}Tl_2$.
Thallic chloride, ...	$\mathbf{Tl}'''Cl_3$.

History.—Thallium was discovered by Crookes in 1861, while examining spectroscopically a seleniferous deposit from a sulphuric acid

manufactory in the Harz. It was at first supposed to be a non-metal, allied to sulphur. In 1862 it was discovered independently by Lamy, who first recognized its metallic character and succeeded in isolating it.

The name *thallium*, derived from θαλλός, a green twig, was given to this element in allusion to the bright green line which constitutes its visible spectrum and by means of which it was discovered.

Occurrence.—Thallium occurs widely distributed in nature, but only in small quantities. Certain varieties ef pyrites—notably Belgian, Westphalian, and Spanish pyrites—contain traces of thallium, and when such pyrites is burnt in the manufacture of sulphuric acid, the thallium condenses and collects in the form of thallous oxide, along with arsenious anhydride and other substances, as a fine dust in the flues of the pyrites burners. Salts of thallium occur in minute quantity in some mineral springs. As an essential constituent, it is found only in the rare mineral *crookesite*, a selenite of copper, silver, and thallium, containing from 16 to 18 per cent. of the latter metal.

Preparation.—When the flue dust containing thallium is treated with dilute sulphuric acid, the thallium goes into solution as thallous sulphate, SO_2Tlo_2, and may be precipitated as sparingly soluble thallous chloride by the addition of hydrochloric acid to the filtered solution. The washed chloride is separated and reconverted into sulphate by treatment with sulphuric acid, heating to expel the hydrochloric acid. The sulphate is purified by crystallization, and from the solution of the pure sulphate metallic thallium is obtained by electrolysis or by precipitation with zinc. The metal, which is thus deposited in soft laminar crystals or as a spongy mass, may be obtained in a coherent form by fusion in a covered crucible under potassic cyanide.

Properties.—Thallium is a heavy metal, white like tin, and soft enough to be scratched with the finger-nail. It may be distilled at a white heat in a current of hydrogen. When exposed to the air it tarnishes superficially, and is converted into thallous oxide. It does not decompose water below a red heat, and is best preserved in closed vessels under water. With access of air it slowly dissolves in water, with formation of thallous hydrate, which in solution absorbs carbonic anhydride, and is ultimately converted into carbonate. Dilute acids readily dissolve it. It is precipitated in the metallic state from its solutions by zinc, but it precipitates lead, copper, mercury, and silver from the solutions of their salts.

Thallium forms two classes of compounds—thallous compounds, in which the metal is monadic, and thallic compounds, in which it is triadic. The members of the first class are the most numerous and best characterized.

COMPOUNDS OF THALLIUM WITH THE HALOGENS.

a. Thallous Compounds.

THALLOUS CHLORIDE, TlCl, *Molecular volume* $\square\square$.—This compound is obtained as a curdy precipitate when hydrochloric acid is added to a

not too dilute solution of thallous hydrate or a thallous salt. It is colored violet by exposure to light. It is soluble in 360 parts of water at ordinary temperature, in from 50 to 60 parts at 100° C. (212° F.). From the hot saturated aqueous solution it crystallizes in cubes. It is less soluble in water containing hydrochloric acid than in pure water. It is readily fusible, yielding a yellow liquid, which solidifies to a white crystalline mass. At higher temperatures it volatilizes.

Thallous bromide, $TlBr$, forms a yellow precipitate. It is less soluble in water than the chloride, which it closely resembles.

Thallous iodide, TlI, is precipitated as a yellow crystalline powder when potassic iodide is added to the solution of a thallous salt. It is almost insoluble in water. Exposure to sunlight colors it green. It is readily fusible, and solidifies to a red crystalline mass, which becomes yellow on standing. At a higher temperature it may be sublimed with partial decomposition.

Thallous fluoride, TlF, is prepared by dissolving thallous carbonate in hydrofluoric acid and evaporating. It crystallizes in colorless, very lustrous anhydrous octahedra, or, with water of crystallization, in hexagonal plates. It dissolves readily in water, and is fusible and volatile. When exposed to sunlight it becomes dark-colored. Solutions containing an excess of hydrofluoric acid deposit on evaporation over sulphuric acid *in vacuo* regular crystals of an acid fluoride, TlF,HF.

b. Thallic Compounds.

Thallic chloride, $TlCl_3$, is formed when thallous chloride is suspended in water and chlorine passed into the liquid. On evaporation *in vacuo* colorless deliquescent prisms of the formula $TlCl_3,OH_2$ are deposited.

Chlorides of thallium intermediate between thallous and thallic chloride are known. In these the thallium is in the triadic condition:

Tetrathallic hexachloride, $\left\{\begin{matrix} Tl(Tl'''Cl_2)Cl \\ Tl(Tl'''Cl_2)Cl \end{matrix}\right.$, is formed when metallic thallium is strongly heated in a current of chlorine. A yellowish-brown mass is thus obtained, sparingly soluble in cold, but readily soluble in boiling water, and crystallizing from the solution in yellow laminæ.

Dithallic tetrachloride, $\left\{\begin{matrix} TlCl_2 \\ TlCl_2 \end{matrix}\right.$.—When metallic thallium or thallous chloride is cautiously heated in chlorine, a compound of the above composition is obtained, which, on heating more strongly, parts with chlorine, and is converted into tetrathallic hexachloride.

Thallic bromide, $TlBr_3$, and *thallic iodide*, TlI_3, are also known. They resemble the chloride, but are less stable.

COMPOUNDS OF THALLIUM WITH OXYGEN AND HYDROXYL.

Thallous oxide, . . .	OTl_2.	$Tl—O—Tl$.
Thallic oxide, ...	$\left\{\begin{matrix} TlO \\ O \\ TlO \end{matrix}\right.$.	$\begin{array}{c} Tl=O \\ \vert \\ O \\ \vert \\ Tl=O \end{array}$.
Thallous hydrate, . .	$TlHo$.	$Tl—O—H$.
Thallic oxyhydrate, . .	$TlOHo$.	$O=Tl—O—H$.

THALLOUS OXIDE, OTl_2.—Metallic thallium when exposed to the air tarnishes, owing to the formation of a coating of thallous oxide.

The oxide may be obtained pure by heating the hydrate to 100° C. (212° F.) with exclusion of air. It forms a black powder which fuses at 300° C. (572° F.) to a dark-yellow liquid. It attracts moisture from the air, and dissolves in water with formation of thallous hydrate.

THALLIC OXIDE, Tl_2O_3.—This oxide is formed when thallium burns in oxygen, and may also be obtained by heating thallic oxyhydrate to 100° C. (212° F.). It is a dark-red powder, insoluble in water. At a red heat it evolves oxygen, and is converted into thallous oxide. Hot concentrated sulphuric acid dissolves it with evolution of oxygen and formation of thallous sulphate. When acidulated water is electrolyzed, employing a positive electrode of thallium, the metal becomes covered with a black deposit of thallic oxide.

THALLOUS HYDRATE, TlHo, is formed when thallium is simultaneously acted upon by water and air or oxygen. It is most readily obtained pure by precipitating thallous sulphate with baric hydrate and evaporating the filtrate. It crystallizes in colorless or faint-yellow rhombic prisms, having the composition $TlHo,OH_2$. It is readily soluble in water and in alcohol, yielding powerfully alkaline solutions. The brown stain which it produces upon turmeric paper disappears, however, after a time, owing to a peculiar destructive action which the hydrate exercises upon the coloring matter. Thallous hydrate is converted at 100° C., or *in vacuo* at ordinary temperatures, into thallous oxide.

Thallic oxyhydrate, **TlOHo**.—This compound is produced as a brown precipitate when freshly precipitated thallous chloride is warmed with a solution of sodic hypochlorite. It is also formed by the action of a caustic alkali upon thallic chloride. It is a brown powder, which at 100° C. (212° F.) is converted into thallic oxide.

OXY-SALTS OF THALLIUM.

a. Thallous Salts.

Thallous nitrate, NO_2Tlo.—This salt is obtained by dissolving the metal in nitric acid. The solution deposits opaque white rhombic prisms, soluble in about 10 parts of water at the ordinary temperature, very readily soluble in boiling water. It fuses without decomposition about 205° C; but is decomposed at a higher temperature.

Thallous carbonate, $COTlo_2$, is formed when a solution of thallous hydrate, or metallic thallium moistened with water, is exposed to the air. It is best prepared by saturating a solution of the hydrate with carbonic anhydride and evaporating to the crystallizing point. It is deposited from the aqueous solution in long, lustrous monoclinic prisms. It dissolves in 20 parts of cold water, yielding a solution with an alkaline reaction. It is fusible without decomposition, but at higher temperatures evolves carbonic anhydride.

Thallous sulphate, SO_2Tlo_2, crystallizes in rhombic prisms, and is isomorphous with potassic sulphate. It is soluble in 20 parts of water at ordinary temperatures and in 5 parts at 100° C. (212° F.).

When air is excluded, it fuses at a red heat without decomposition; but when heated in air, it is decomposed with evolution of sulphurous anhydride.—*Hydric thallous sulphate* is deposited from solutions containing a large excess of sulphuric acid. It crystallizes in short thick prisms, having the formula $SO_2HoTlo,3OH$.—With the sulphates of the dyad metals thallous sulphate forms double salts, such as the double sulphate of zinc and thallium, $\left\{\begin{matrix} SO_2Tlo \\ Zno'' \\ SO_2Tlo \end{matrix}\right. ,6OH_2$, corresponding with the double sulphates of ammonium and potassium with the dyad metals, and like these, containing 6 molecules of water of crystallization.

Thallous phosphate, $POTlo_3$, is obtained as a white crystalline precipitate when a thallous salt is added to a solution of ordinary sodic phosphate containing ammonia. It dissolves in 200 parts of cold and in 150 parts of boiling water. It is soluble in solutions of ammonia salts.—*Hydric dithallous phosphate*, $POHoTlo_2,OH_2$, is prepared by neutralizing a solution of phosphoric acid with thallous carbonate. The solution deposits on evaporation rhombic crystals, which part with their water of crystallization at 200° C, and at a red heat are converted into a vitreous mass of *thallous pyrophosphate*, $P_2O_3Tlo_4$.—*Dihydric thallous phoshate*, $POHo_2Tlo$, is prepared by adding to a solution of thallous carbonate sufficient phosphoric acid to produce a distinctly acid reaction, and then evaporating. It forms nacreous monoclinic prisms or laminæ, readily soluble in water. At a red heat it is converted into metaphosphate.

b. Thallic salts.

Thallic nitrate, $\left\{\begin{matrix} NO_2- \\ NO_2-Tlo''' \\ NO_2- \end{matrix}\right. ,8OH_2$, is deposited in colorless crystals from the solution of the thallic oxide in concentrated nitric acid. Excess of water decomposes the salt with separation of thallic oxyhydrate.

Thallic sulphate, $S_3O_6Tlo'''_2,7OH_2$, crystallizes in thin colorless laminæ from a solution of thallic oxide or hydrate in warm dilute sulphuric acid. Water decomposes it in the cold. When heated it gives off sulphuric acid, sulphuric anhydride, and oxygen, and is converted into thallous sulphate.

COMPOUNDS OF THALLIUM WITH SULPHUR.

Thallous sulphide, STl_2.—This compound is obtained as a brownish-black amorphous precipitate when sulphuretted hydrogen is passed into an alkaline or acetic acid solution of a thallium salt. From a solution of thallous sulphate containing a trace of free sulphuric acid, it is deposited in minute, lustrous, dark-blue tetrahedra. It may be obtained as a black, lustrous, crystalline mass by fusing thallium with sulphur in absence of air.—Thallous sulphide is insoluble in water, in alkalies, or alkaline sulphides, and in potassic cyanide, soluble with difficulty in acetic acid, readily soluble in sulphuric and in nitric acid. The precipitated sulphide, when exposed to the air in a moist state, undergoes oxidation to sulphate. By heating in a current of hydrogen, thallous sulphide is reduced to metallic thallium.

Thallic sulphide, $Tl_2S''_3$, is prepared by fusing thallium with an excess of sulphur, expelling this excess at a low temperature with exclusion of air. It is a black amorphous readily fusible substance. In warm weather it is soft like pitch, but below 12° C.

it is brittle. Hot dilute sulphuric acid dissolves it without separation of sulphur Thallic sulphide is the anhyride of a sulpho-acid, $TlS''Hs$. The potassium salt of this acid, *potassic sulphothallate*, $TlS''Ks$, is obtained by fusing together 1 part of thallous sulphate with 6 parts of potassic carbonate and 6 parts of sulphur, extracting the cooled mass with water. The sulphothallate remains behind as a dark cochineal-red powder, consisting of microscopic quadratic plates.

General Properties and Reactions of the Compounds of Thallium.—The salts of thallium are generally colorless. They have a disagreeable metallic taste and are poisonous. *Zinc* precipitates metallic thallium from solutions of the salts. *Sulphuretted hydrogen* precipitates neutral or slightly acid solutions of thallium salts only partially, and solutions containing an excess of a mineral acid not at all. *Ammonic sulphide* precipitates the whole of the thallium as brownish-black thallous sulphide, insoluble in alkaline sulphides. Thallous salts yield precipitates with the *hydracids* and soluble *haloid salts* (see p. 558). Thallium compounds impart to the non-luminous flame a magnificent emerald-green coloration. The spectrum of the thallium flame consists of one bright green line.

INDIUM, In_2?

Atomic weight = 113.4. *Probable molecular weight* = 226.8. *Sp. gr.* 7.3 *to* 7.4. *Fuses at* 176° C. (348.8° F.). *Atomicity* '''. *Evidence of atomicity:*

Indic chloride, ... $In'''Cl_3$.
Indic hydrate, ... $In'''Ho_3$.

History.—Indium was discovered in the year 1863 by Reich and Richter in the zinc blende of Freiberg by means of the spectroscope. It received its name from the characteristic indigo-blue line which its spectrum exhibits.

Occurrence.—Indium occurs in minute traces in various zinc blendes, particularly in that of Freiberg. The best source of the metal is the zinc from Freiberg, which contains on an average 0.05 per cent. of indium.

Preparation.—Freiberg zinc is treated with a quantity of dilute hydrochloric acid or sulphuric acid not quite sufficient to dissolve it, and is boiled with the liquid until gas ceases to be evolved. In this way any indium which may have gone into solution is precipitated upon the undissolved zinc. The spongy metallic mass which remains, and which, in addition to indium and zinc, usually contains lead, arsenic, cadmium, copper, tin, and iron, is dissolved in nitric acid and the solution boiled down with sulphuric acid until all the nitric acid is expelled, after which it is diluted with water, filtered from plumbic sulphate, and precipitated with a large excess of ammonia. The precipitate, which contains all the indium and iron, along with traces of the other metals present, is washed, dissolved in a small quantity of hydrochloric acid, and, after adding hydric sodic sulphite, boiled until the smell of sulphurous anhy-

dride has disappeared. In this way the whole of the indium is precipitated as basic indic sulphite hydrate (see Indic Sulphite). It is, however, still contaminated with lead, and, in order to free it from this impurity, it is dissolved in aqueous sulphurous acid, separated by filtration from undissolved plumbic sulphite and reprecipitated by boiling, when the pure basic sulphite is obtained. In order to prepare metallic indium, the sulphite is dissolved in hot hydrochloric acid, the solution precipitated with ammonia, and the precipitate of indic hydrate ignited and afterwards reduced in a current of hydrogen.

Properties.—Indium is a non-crystalline, silver-white, lustrous metal. It is softer than lead and very malleable. It undergoes no change in air at ordinary temperatures, but when strongly heated in air, burns with a blue flame, giving off a brown smoke of indic oxide which condenses on a cold surface as a yellow incrustation. Water, even at its boiling-point, is without action upon the metal. Dilute hydrochloric and sulphuric acids dissolve it slowly with evolution of hydrogen; nitric acid dissolves it readily.

COMPOUNDS OF INDIUM WITH THE HALOGENS.

Indic chloride, $InCl_3$.—*Molecular volume* $\square\square$.—This compound is prepared by heating the metal, or a mixture of the oxide with carbon, in a current of chlorine. It sublimes, without previous fusion, in soft, colorless laminæ. It is deliquescent, and hisses when thrown into water, evolving great heat. The solution may be evaporated on the water-bath without decomposition, but on heating to a higher temperature to expel the last traces of water, hydrochloric acid is evolved and oxychlorides are formed.

The bromide and iodide, which resemble the chloride in their properties, may be obtained by the direct union of their elements.

COMPOUNDS OF INDIUM WITH OXYGEN AND HYDROXYL.

$$\text{Indic oxide,} \quad \ldots \quad \left\{\begin{array}{l} InO \\ O \\ InO \end{array}\right. . \qquad \begin{array}{c} In{=}O \\ | \\ O \\ | \\ In{=}O \end{array} .$$

$$\text{Indic hydrate,} \quad \ldots \quad InHo_3. \qquad In\begin{array}{l} \diagup O{-}H \\ {-}O{-}H \\ \diagdown O{-}H \end{array} .$$

Indic oxide, In_2O_3, is formed as a pale yellow powder when the metal is burned in air or oxygen. It may be prepared by heating the hydrate or the nitrate. When heated it becomes reddish-brown, but recovers its original color on cooling.—By heating the oxide to 300° C. (572° F.) in a current of hydrogen a black powder is obtained which, unless

allowed to cool thoroughly before bringing it in contact with air, is pyrophoric. It appears to contain the lower oxide $'In''_2O_2$.

Indic hydrate, $InHo_3$, is obtained as a white gelatinous precipitate when ammonia is added to the solution of an indium salt. After drying at 100° C. it forms a white horny mass, which at a higher temperature is converted into the oxide. The freshly precipitated hydrate is soluble in excess of potash and soda, but not in ammonia. It separates from the alkaline solution, slowly on standing, rapidly on boiling, or on the addition of ammonic chloride.

OXY-SALTS OF INDIUM.

Indic nitrate, $N_3O_6Ino''',4OH_2$, crystallizes from its neutral aqueous solution with difficulty. From solutions containing an excess of nitric acid it is deposited in tufts of deliquescent needles.

Indic sulphate, $S_3O_6Ino'''_2$, does not crystallize. By evaporation of its solution to dryness and heating to 100° C. (212° F.) it is obtained as a gummy mass having the composition $S_3O_6Ino'''_2,9OH_2$; this when heated to 300° C. (572° F.) is converted into the anhydrous salt. When a solution of indic sulphate containing an excess of sulphuric acid is evaporated *in vacuo*, deliquescent crystals of *dihydric di-indic tetrasulphate*, $S_4O_8Ho_2In'''_2,8OH_2$, are deposited

Diammonic di-indic tetrasulphate (*Indium ammonia alum*). $S_4O_8(NH_4O)_2Ino'''_2\ 24OH_2$, crystallizes from mixed solutions of indic and ammonic sulphates in well-defined, colorless, regular octahedra. These dissolve in half their weight of water at 16° C., and in a quarter of their weight at 30° C. (86° F.). At 36° C. (96.8° F.) the crystals fuse in their water of crystallization, and from the solution an octo-aquate is deposited in monoclinic crystals. Similar octo-aquates of the double sulphates of indium with sodium and potassium have also been prepared, but the aquates with 24 aq., or alums, are not known.

Indic sulphite.—A basic indic sulphite of the formula $S_3O_3(O_2InHo)''_2(OInHo_2)_2,5OH_2$, *tetrindic trisulphite hexahydrate*, is deposited as a white crystalline powder when the solution of an indium salt is boiled with hydric sodic sulphite. It is insoluble in water, but readily soluble in acids. It dissolves in aqueous sulphurous acid, but is reprecipitated from this solution by boiling. This property is turned to account in the separation of indium from other metals (p. 562).

COMPOUNDS OF INDIUM WITH SULPHUR.

Indic sulphide, $In_2S''_3$, is obtained as a brown infusible mass by the direct union of its elements at a red heat. It is precipitated as an amorphous yellow powder when sulphuretted hydrogen is passed into the solution of an indium salt, but the precipitation is complete only when the liquid is kept neutral during the whole operation, or when sodic acetate has been added.—Ammonic sulphide produces in solutions of indium salts a white precipitate of a sulphhydrate which dissolves in an excess of the precipitant on heating and separates out again on cooling.—Indic sulphide is the anhydride of a sulpho-acid, *sulphindic acid*, $InS''Hs$. *Potassic sulphindate*, $InS''Ks$, is prepared by heating together 1 part of indic oxide, 6 parts of potassic carbonate, and 6 parts of sulphur, at first at a gentle heat, afterwards more strongly On extracting the cooled mass with water the sulphindate remains behind in the form of bright hyacinth-red, quadratic plates. Acids readily decompose it.

General Properties and Reactions of the Compounds of Indium.—The salts of indium with colorless acids are colorless. *Zinc* precipitates the metal from the solutions of its salts. *Caustic alkalies* precipitate white gelatinous indic hydrate, slightly soluble in excess, but reprecipitated on boiling. *Sulphuretted hydrogen* gives no precipitate in solutions containing an excess of mineral acid; from acetic acid solution indic sulphide is precipitated. The same precipitate is produced

by *ammonic sulphide.* The compounds of indium color the non-luminous flame dark-blue. The spectrum exhibits an intense line in the indigo and a less marked line in the violet.

CHAPTER XXXVI.

TETRAD ELEMENTS.

SECTION II.

ALUMINIUM, Al.

Atomic weight = 27. *Molecular weight unknown. Sp. gr.* 2.67. *Fuses about* 700° C. (1292° F.). *Atomicity* ^{iv}, *but is always a pseudo-triad. Evidence of atomicity : analogy of iron and chromium.*

History.—Aluminium was first isolated by Wöhler in the year 1827, but it was first obtained in the massive form by Deville in 1854.

Occurrence.—Aluminium is, with the exception of oxygen and silicon, the most abundant and widely distributed of the elements. It is always found in combination with oxygen. The oxide $\mathbf{Al}_2O_3$ occurs as *corundum, ruby,* or *sapphire ;* the hydrate as *hydrargillite, diaspore,* and *bauxite ;* whilst the compound silicates of aluminium with other metals form a vast number of important minerals which are among the proximate constituents of the various rocks (see Silicates, p. 319).

Preparation.—Aluminium cannot be reduced directly from its oxide. It may be obtained by passsing the vapor of the chloride over heated potassium or sodium, and by the electrolysis of fused sodic aluminic chloride, $\mathbf{Al}_2Cl_6,2NaCl$. On a large scale aluminium is prepared from bauxite, a native aluminic oxyhydrate of the formula $\mathbf{Al}_2OHo_4$, in which a portion of the aluminium is isomorphously replaced by iron. This mineral contains about 50 per cent. of alumina. When heated with caustic soda in a reverberatory furnace the alumina forms sodic aluminate, $\mathbf{Al}_2O_2Nao_2$, which can be extracted with water, whilst the iron remains behind as insoluble ferric oxide. By passing carbonic anhydride through the solution of the aluminate, aluminic hydrate is precipitated, which by drying and heating is converted into alumina. This is mixed with powdered coal and common salt, and the mixture is made into balls, which are introduced into a fire-clay retort and heated to whiteness, while a current of dry chlorine is passed over them. The following reaction occurs:

$$\underset{\text{Alumina.}}{\mathbf{Al}_2O_3} + 3C + 3Cl_2 = \underset{\substack{\text{Aluminic}\\\text{chloride.}}}{\mathbf{Al}_2Cl_6} + \underset{\substack{\text{Carbonic}\\\text{oxide.}}}{3CO}.$$

The aluminic chloride volatilizes along with the sodic chloride as sodic aluminic chloride, which is condensed. It is now only necessary to

reduce this double chloride with sodium. For this purpose the double chlorides is heated with sodium and cryolite (a native sodic aluminic fluoride of the formula $\mathbf{Al_2F_6,6NaF}$), this last acting as a flux. In practice 100 kilos. of the double chloride, 35 kilos. of sodium, and 40 kilos. of cryolite are employed in one operation. This mixture is heated, with gradual rise of temperature, on the hearth of a reverberatory furnace. The reduced aluminium fuses and collects on the hearth, whence it is drawn off and cast into ingots. The metal thus obtained contains iron and silicon.

Aluminium may also be prepared from cryolite by mixing the finely powdered mineral with sodic and potassic chloride and heating the mixture in a crucible with sodium. The yield by this method is small and the metal impure.

Properties.—Aluminium is a white metal, closely resembling zinc in color and hardness. It may be rolled into very thin foil or drawn into fine wire, and possesses at the same time great tenacity. It is most readily worked at a temperature between 100° C. (212° F.) and 150° C. (302° F.). It is not volatile at the highest temperatures that can be artificially produced. It is not oxidized by exposure to the air at ordinary temperatures, and is only superficially oxidized when fused in oxygen; but in the form of foil or wire it may be burnt in oxygen, and emits a dazzling white light. Aluminium, when pure, does not decompose water, even at a red heat, but does so at 100° C. (212° F.) if the aluminium contains traces of sodium. It is soluble in caustic alkaline solutions and in hydrochloric and sulphuric acids. Nitric acid in all degrees of concentration is without action upon it. Organic acids alone scarcely attack it, but dissolve it rapidly in presence of chlorides, such as common salt; a fact which precludes its employment in the manufacture of utensils which have to come in contact with food.

Uses.—Its lightness, tenacity, unalterability in air, and other valuable properties, together with the abundance of its occurrence in nature, would probably render aluminium one of the most useful of metals, were it not for the difficulties attending its production in large quantity. For many purposes it might, for example, replace zinc and iron. At present, however, it is chiefly used in the manufacture of various physical instruments, especially beams of delicate balances, in which a combination of lightness and inflexibility is essential.

Aluminium bronze.—Aluminium forms alloys with most of the other metals; those with copper are the most important. *Aluminium bronze* is an alloy containing 90 parts of copper to 10 parts of aluminium, and is prepared by fusing the two metals together. Electrolytic copper is generally employed for this purpose, the quality of the alloy being dependent on the purity of the copper. The presence of iron is especially prejudicial. The alloy is brittle at first, but by repeated fusion becomes malleable. It has the color of gold, and resists the action of the air. It yields sharp castings, and is more easily worked than steel. Its tenacity is equal to that of cast steel, and more than twice that of gun-metal, whilst its resistance to flexure is thrice that of gun-metal. It is employed in the manufacture of imitation gold ornaments and of physical instruments.

Alloys of aluminium with silver and with tin have also found application in the arts.

COMPOUNDS OF ALUMINIUM WITH THE HALOGENS.

ALUMINIC CHLORIDE, $\mathbf{Al}_2Cl_6$.—*Molecular volume* $\square\square$.—This compound is formed when aluminium is heated in chlorine. (Preparation, see p. 564.)—If contaminated with ferric chloride, which imparts to it a yellow color, it may be purified by mixing it with iron filings, or better with aluminium filings, and re-subliming. In either case the ferric chloride is converted into the much less volatile ferrous chloride. Aluminic chloride when perfectly pure is a white crystalline substance. It sublimes readily at ordinary pressures without fusing, but may be fused under the pressure of its own vapor, or when rapidly heated in large quantity. By sublimation it is sometimes obtained in hexagonal tabular crystals. It attracts moisture from the air, and evolves hydrochloric acid. The solution of the metal or the oxide in hydrochloric acid deposits on concentration colorless needle-shaped crystals of the aquate $\mathbf{Al}_2Cl_6,12\mathbf{O}H_2$, which on heating are decomposed into water, hydrochloric acid, and alumina. Aluminic chloride forms a large number of compounds with the chlorides of other elements. *Potassic aluminic chloride*, $\mathbf{Al}_2Cl_6,2KCl$, and *sodic aluminic chloride*, $\mathbf{Al}_2Cl_6,2NaCl$, are formed when aluminic chloride is heated with potassic and sodic chlorides. The sodium compound fuses without decomposition at 185° C. (365° F.), and is volatile at a red heat. It is employed in the preparation of aluminium.

Aluminic bromide, $\mathbf{Al}_2Br_6$.—*Molecular volume* $\square\square$.—Aluminium and bromine unite with incandescence to form this compound. It may be most readily obtained by passing bromine vapor over a red-hot mixture of alumina and carbon. It may be purified by repeated sublimation with aluminium in a sealed tube. It forms deliquescent, colorless, lustrous laminæ, fusing at 90° C. (194° F.), and boiling between 265° C. (509° F.) and 270° C. (518° F.). Concentrated aqueous solutions deposit colorless needles of the aquate $\mathbf{Al}_2Br_6.12\mathbf{O}H_2$, which on heating are decomposed like the corresponding chlorine compound. Aluminic bromide forms fusible double bromides with the bromides of the alkali metals: thus, *potassic aluminic bromide*, $\mathbf{Al}_2Br_6,2KBr$.

Aluminic iodide, $\mathbf{Al}_2I_6$.—*Molecular volume* $\square\square$.—This compound is formed with incandescence when aluminium and iodine are cautiously heated together in a sealed tube. It is also formed when argentic iodide is heated with aluminium filings.—Aluminic iodide is a white crystalline mass, fusing at 185° C. (365° F.), and boiling at 360° C. (680° F.). Its vapor is combustible, and forms an explosive mixture with air. The products of combustion are alumina and iodine. It is decomposed in the same way when heated in contact with air. When exposed to the air it fumes and deliquesces. It is readily soluble in water, alcohol, and bisulphide of carbon. It forms an aquate, $\mathbf{Al}_2I_6.12\mathbf{O}H_2$, and unites with the alkaline bromides to form double iodides, all of which compounds closely resemble the corresponding chlorides and bromides.

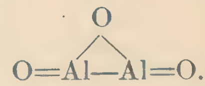
Aluminic fluoride, $\mathbf{Al}_2F_6$, is formed by the action of gaseous or aqueous hydrofluoric acid upon alumina or aluminic hydrate. At a bright red heat it sublimes in colorless rhombohedra, closely approximating to cubes. It is insoluble in water, and is not decomposed by acids.—Aluminic fluoride forms insoluble double fluorides with the fluorides of the alkali metals. The most important is *aluminic sodic fluoride*, $\mathbf{Al}_2F_6,6NaF$, which occurs as the mineral *cryolite* in enormous deposits on the coast of Greenland. It may be artificially obtained by fusing together its component fluorides. It forms a white, translucent mass. It is decomposed by sulphuric acid with evolution of hydrofluoric acid. Boiling with caustic alkalies, or with calcic hydrate and water, also decomposes it. In the decomposition with calcic hydrate insoluble calcic fluoride is formed, whilst sodic aluminate goes into solution:

$$\underset{\text{Sodic aluminic fluoride.}}{\mathbf{Al}_2F_6,6NaF} + \underset{\text{Calcic hydrate.}}{6\mathbf{Ca}Ho_2} = \underset{\text{Calcic fluoride.}}{6\mathbf{Ca}F_2} + \underset{\text{Sodic aluminate.}}{\mathbf{Al}_2Nao_6} + \underset{\text{Water.}}{6\mathbf{O}H_2}.$$

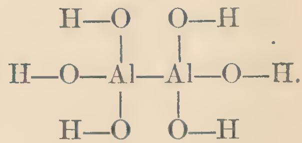
On this reaction is based an industrial process for the preparation of soda and aluminium salts from cryolite.

COMPOUNDS OF ALUMINIUM WITH OXYGEN AND HYDROXYL.

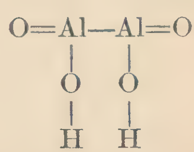
Aluminic oxide (*Alumina*), $\left\{\begin{matrix} AlO \\ AlO \end{matrix}\right. O.$



Aluminic hydrate (*Hydrargillite*), $\left\{\begin{matrix} AlHo_3 \\ AlHo_3 \end{matrix}\right..$



Aluminic oxydihydrate (*Diaspore*) $\left\{\begin{matrix} AlOHo \\ AlOHo \end{matrix}\right..$



ALUMINIC OXIDE (*Alumina*), Al_2O_3.—This oxide occurs native in hexagonal crystals, sometimes colorless, sometimes variously colored owing to the presence of other oxides. Crystallized alumina is harder than any known substance with the exception of the diamond and crystallized boron. The colorless or gray crystals are known as *corundum;* the red crystals, the color of which is due to chromium, constitute the gem *ruby;* whilst *sapphires* are crystals of alumina colored blue, probably by cobalt. In an impure state, contaminated with iron and silica, alumina occurs in large masses as *emery*. The latter mineral, when powdered and levigated, is employed for grinding and polishing surfaces of glass and metal, purposes for which from its hardness it is admirably suited. Alumina is obtained as a white amorphous powder by heating the hydrate or ammonia alum; in the latter case it is difficult to expel the last traces of sulphuric acid. It may be obtained in the crystallized condition by the action of aluminic fluoride upon boric anhydride at a high temperature. Fremy and Feil have prepared crystallized alumina on a large scale by heating together equal weights of alumina and red-lead in a clay crucible to bright redness for a considerable time, sometimes as much as twenty days. The cooled mass consisted of two layers: one a vitreous mass of plumbic silicate, the silica of which had been derived from the material of the crucible; the other crystalline, and containing cavities which were filled with well-formed crystals of corundum. By the addition of from 2 to 3 per cent. of potassic dichromate to the above mixture crystals of ruby were obtained; the color of sapphires was produced by adding a small quantity of cobaltous oxide, together with a trace of potassic dichromate. By heating a mixture of equal weights of alumina and baric fluoride, with a small quantity of potassic dichromate for a length of time to a very high temperature in a glass furnace, magnificent crystals of ruby

were obtained. The reaction in this case depends upon the formation of aluminic fluoride which is then decomposed by the furnace gases. The crystals of ruby are deposited in the upper part of the crucible.—Crystallized or strongly ignited alumina is insoluble in acids at ordinary pressures, but dissolves in concentrated sulphuric acid when heated with it in sealed tubes. It is also attacked by fusion with hydric potassic sulphate or potassic hydrate, after which treatment it dissolves in water. Alumina is fusible in the oxyhydrogen flame.

Aluminic hydrate, $\mathbf{Al}_2Ho_6$, occurs as *hydrargillite* in small hexagonal crystals. When ammonia is added to the solution of an aluminium salt a white gelatinous precipitate is formed, which after drying at ordinary temperatures has the composition $\mathbf{Al}_2Ho_6 2\mathbf{O}H_2$. This when heated slightly above 300° C., is converted into *aluminic oxydihydrate*, $\mathbf{Al}_2O_2Ho_2$, a compound which occurs in nature as the mineral *diaspore* in rhombic crystals. An aluminic oxyhydrate, corresponding with the formula $\mathbf{Al}_2OHo_4$, *aluminic oxytetrahydrate*, occurs as the mineral *bauxite*, but a portion of the aluminium in this compound is isomorphously replaced by iron. All the aluminic hydrates are converted into the oxide by heating.—Aluminic hydrate is insoluble in ammonia, but when freshly precipitated dissolves readily in acids and in solutions of potassic and sodic hydrate. When dried by a moderate warmth, or when allowed to stand under water, it becomes difficultly soluble in acids and alkalies.—Freshly precipitated aluminic hydrate dissolves in a solution of aluminic chloride, and if the liquid thus obtained be subjected to dialysis, hydrochloric acid passes through the dialyser, till at last only a neutral tasteless solution of colloidal aluminic hydrate remains. This soluble modification of aluminic hydrate is very unstable: the solution coagulates after standing for some days, and the same change takes place immediately on the addition of traces of acids, alkalies, or salts. Aluminic hydrate possesses the property of precipitating organic coloring matters from their solutions. Upon this property the application of the salts of alumina as mordants in dyeing and in the preparation of the so-called *lakes* depends.

Aluminates.—Aluminic oxydihydrate behaves towards stronger bases like a weak acid. Its salts, in which both the hydrogen-atoms of the oxydihydrate are replaced by metal, are known as *aluminates*. The aluminates of potassium and sodium are prepared by dissolving aluminic hydrate in caustic potash or soda; by evaporation *in vacuo*, the potassic aluminate may be obtained in hard lustrous crystals of the formula $\mathbf{Al}_2O_2Ko_2,3\mathbf{O}H_2$. *Sodic aluminate*, $\mathbf{Al}_2O_2Nao_2$, has not been obtained in the crystallized state. It is used as a mordant. *Beryllic aluminate*, $\mathbf{Al}_2O_2Beo''$, occurs in nature as the mineral *chrysoberyl* in green rhombic crystals. The aluminates of the metals of the magnesium group occur in nature as the *spinelles*, crystallized in forms belonging to the regular system. Examples of these are: *magnesic aluminate* or *spinelle*, $\mathbf{Al}_2O_2Mgo''$, and *zincic aluminate* or *zinc spinelle*, $\mathbf{Al}_2O_2Zno''$. The two latter compounds may be prepared artificially by passing the vapor of aluminic chloride over strongly heated magnesia or zincic oxide, or by heating alumina and boric anhydride with these oxides to a white heat for several days.

OXY-SALTS OF ALUMINIUM.

Aluminic nitrate, $\mathbf{N}_6O_{12}('\mathbf{Al}'''_2O_6)^{vi},18\mathbf{O}H_2$, crystallizes from a concentrated solution of the hydrate in nitric acid in deliquescent monoclinic prisms. On heating to 150° C. (302° F.) the salt is decomposed, leaving a residue of alumina. It is employed in calico-printing as a mordant.

ALUMINIC SULPHATE, $S_3O_6('Al'''_2O_6)^{vi},18OH_2$, occurs as the mineral *keramohalite.* It is prepared on a large scale by dissolving aluminic hydrate, obtained from cryolite or bauxite and as free from iron as possible, in sulphuric acid; or by decomposing china clay, a hydrated aluminic silicate, with sulphuric acid. The solution is evaporated till it solidifies on cooling. A soft mass is thus obtained which is cut into blocks. It is difficultly crystallizable, and forms thin, flexible, nacreous laminæ. It dissolves in twice its weight of cold water. When heated, it first fuses in its water of crystallization, then swells up, and is converted into a white porous mass of the anhydrous salt. Aluminic sulphate is employed as a mordant and in weighting paper.—Basic sulphates are formed when a solution of the normal sulphate is precipitated with an insufficiency of ammonia, or by boiling its solution with the freshly precipitated hydrate. A compound of this class, *aluminic sulphate tetrahydrate,* $SO_2('Al'''_2O_2Ho_4)'',7OH_2$, occurs in nature as the mineral *aluminite.*

THE ALUMS.

Among the most important salts of alumina are the double sulphates which it forms with the alkalies, known as the alums. Of these the principal are potash alum or common alum, *dipotassic aluminic tetrasulphate,* $\left.\begin{array}{l} SO_2Ko- \\ SO_2- \\ SO_2- \\ SO_2Ko- \end{array}\right]('Al'''_2O_6)^{vi},24OH_2$, and ammonia alum, in which the potassium of the preceding compound is replaced by ammonium. The object of preparing these salts, which are extensively used by the dyer and calico-printer, is to obtain compounds of alumina in a very pure form, and especially as free from iron as possible. The alumina is alone valuable.

The name alum is not restricted to compounds of alumina: it is employed to designate a class of tetrasulphates which, like potash alum, contain in their molecule two atoms of a monad metal (or the equivalent of a monad metal, such as NH_4) together with one hexadic metallic group—of which $'Al'''_2$ may be taken as a type—and which crystallizes with 24 aq. in regular octahedra. Almost any monad metal may enter into the composition of an alum: thus, besides the alums above mentioned, alums have been prepared containing sodium, cæsium, rubidium, silver, and thallium. The hexadic group $'Al'''_2$ may be replaced by the isomorphous groups $'Cr'''_2$, $'Fe'''_2$, and $'Mn'''_2$. It even appears that this group of two pseudo-triads may be replaced by two true triads: thus an ammonia indium alum has been prepared containing the hexadic group In_2 (p. 563).

The following system of nomenclature is as a rule applied to these compounds. If the monad metal be potassium, the name of this metal is not introduced into the name of the compound: thus chrome alum means potassium chromium alum. If the hexadic group be $'Al'''_2$, aluminium is not named: thus by ammonia alum is understood ammonia aluminium alum. If the alum contain neither potash nor aluminium, both metals present must be named: thus, ammonia chrome alum.

Selenic acid forms a similar series of alums. These may be regarded as sulphuric alums in which sulphur has been replaced by the isomorphous selenium. The potash alum of this series has the formula $\left.\begin{array}{l} SeO_2Ko- \\ SeO_2- \\ SeO_2- \\ SeO_2Ko- \end{array}\right]('Al'''_2O_6)^{vi},24OH_2$.

A class of *pseudo alums* also exists in which the two monad atoms are replaced by one dyad atom. These pseudo alums also contain 24 aq. in the molecule, but do not crystallize in the regular system (see Pseudo Alums).

A solution containing two or more octahedral alums deposits octahedral crystals, in which the various alums present may be contained in any proportion.

Potash alum crystallizes from mixed solutions of aluminic and potassic sulphates. It is formed in nature, especially in volcanic districts, by the action of sulphurous acid and oxygen upon rocks containing potassic and aluminic silicates. In the neighborhood of Naples and at Solfatara it occurs in quantity sufficient to render its extraction profitable. Large quantities of very pure alum, the so-called Roman alum, are obtained from the mineral *alum stone* or *alunite*, a basic double silicate of potash and alumina of the formula

$$\begin{array}{l} \mathbf{S}OHoKo \\ \mathbf{S}OHo_2 \\ \mathbf{S}OHo_2 \\ \mathbf{S}OHoKo \end{array} \begin{array}{l} ('Al'''_2Ho_3O_3)''' \\ ('Al'''_2Ho_4O_3)'' \\ ('Al'''_2Ho_3O_3)''' \end{array}$$

, which occurs at Tolfa and in Hungary. The mineral is mixed with fuel and roasted, either in heaps or in kilns, after which it is moistened and exposed to the air for several weeks. The mass gradually disintegrates, and is then extracted with water, when alum goes into solution and alumina remains behind. The liquid is concentrated and allowed to crystallize.—Alum is, however, more frequently prepared from *alum shale*, a bituminous shale containing iron pyrites disseminated through its mass. The shale is exposed in heaps to the air, by which means the iron pyrites ($\mathbf{Fe}S''_2$) is gradually oxidized to ferrous sulphate and sulphuric acid, the latter of which then decomposes the aluminic silicate present in the shale. The process is generally shortened by first roasting the shale, in order to effect a partial oxidation, after which the roasted shale is moistened and exposed to the air as above described. The oxidized shale is lixiviated with water and the solution evaporated. A considerable quantity of the ferrous sulphate present crystallizes out and is removed. If, however, the shale has been exposed to the air for a sufficient length of time, the ferrous sulphate is oxidized to ferric sulphate, the presence of which is less objectionable. The concentrated mother liquor containing aluminic sulphate is now heated to boiling, and solid potassic sulphate is dissolved in it. The potassic sulphate combines with the alumnic sulphate to form alum. If any considerable quantity of ferric sulphate is present it is advantageous to add, along with the potassic sulphate, a quantity of potassic chloride equivalent to the ferric sulphate, the two latter salts yielding by double decomposition potassic sulphate and the very soluble ferric chloride. The presence of ferrous sulphate is objectionable, as a loss of potassium salt is occasioned by the formation of ferrous dipotassic disulphate, $\left\{\begin{array}{l} \mathbf{S}O_2Ko \\ Feo'' \\ \mathbf{S}O_2Ko \end{array}\right.$. The hot solution, which now contains the alum, is well stirred till cold. In this way the alum is deposited in small crystals, which are less apt to retain impurities from the mother liquor than the large crystals which would be formed were the liquid permitted to cool undisturbed. The small crystals, known as *alum meal*, are washed with cold water, dissolved in boiling water, and the solution allowed to crystallize in large

barrels with movable staves, which are afterwards taken to pieces in order to remove the large crystals of alum which line their sides.—Alum crystallizes in large colorless transparent regular octahedra, which as a rule also exhibit subordinate cubical faces. From solutions containing free caustic alkali, or basic alum, the alum crystallizes by spontaneous evaporation in cubical crystals, which have exactly the same composition as octahedral alum. The crystallized alum is soluble in 7 parts of water at 20° C. (68° F.), and in less than $\frac{1}{3}$ part at 100° C. (212° F.). The solution has a faint acid reaction and a sweet astringent taste. The crystals are insoluble in alcohol. When heated they fuse in their water of crystallization, which is expelled by continued heating, leaving a white porous mass known as *burnt alum.* This dissolves slowly in water. Anhydrous alum may be obtained in six-sided crystals by fusing alumina with hydric potassic sulphate, and removing the excess of this salt from the fused mass with hot water.

AMMONIA ALUM (*diammonic aluminic tetrasulphate*),

$$\left.\begin{matrix} \mathbf{S}O_2(NH_4O)- \\ \mathbf{S}O_2- \\ \mathbf{S}O_2- \\ \mathbf{S}O_2(NH_4O)- \end{matrix}\right] ('Al'''_2O_6)^{vi}, 24\mathbf{O}H_2.—$$

This compound was formerly prepared from alum shale by methods similar to those employed in the manufacture of potash alum. The roasted shale was treated with sulphuric acid, and into the acid solution of aluminic sulphate, ammonia, obtained from the ammoniacal liquors of the gas-works, was passed. The alum was purified by crystallization. Since the introduction of cheap potash salts from the Stassfurt beds, the manufacture of ammonia alum in England has practically ceased.—Ammonia alum crystallizes in large colorless octahedral crystals, in appearance indistinguishable from the potash salt. Its solubility is also almost the same as that of potash alum.

Soda alum, $\mathbf{S}_4O_8Nao_2('Al'''_2O_6)^{vi},24\mathbf{O}H_2$, is difficult to purify on account of its great solubility. It dissolves in its own weight of water at ordinary temperatures. It is not manufactured.

ALUMINIC PHOSPHATES.—The normal orthophosphate, *aluminic diphosphate*, $\begin{matrix}PO\\PO\end{matrix}('Al'''_2O_6)^{vi}$, is obtained as a hydrated gelatinous precipitate when hydric disodic phosphate is added to the neutral solution of an aluminium salt. It is soluble in alkalies, but not in ammonia; and in mineral acids, but not in acetic acid.—Various basic phosphates of alumina occur in nature. The mineral *wavellite*, which forms rhombic crystals or radiating masses, is a basic phosphate of the formula $\mathbf{P}_4O('Al'''_2O_6)^{vi}_3,12\mathbf{O}H_2$. *Calaite*, which when colored greenish blue by copper constitutes the gem *oriental turqûoise*, has the formula $\mathbf{P}O('Al'''_2Ho_3O_3)''',\mathbf{O}H_2$.

ALUMINIC SILICATES.—The silicates of alumina, both simple and compound, form a large class of important minerals. A detailed description of these belongs rather to mineralogy than to chemistry; but the names and formulæ of some of the more important may be here given.

Andalusite (*chiastolite cyanite, fibrolite, sillimanite*), ... $SiO('Al'''_2O_4)''$.

Bucholzite (*xenotime*), ...
$$\begin{array}{l} Si \\ Si \\ Si \end{array} \begin{array}{l} ('Al'''_2O_6)^{vi} \\ ('Al'''_2O_6)^{vi} \end{array}$$

Miloschine, ... $SiHo_2('Al'''_2Ho_4O_2)''$.

Alophane, ... $SiHo_2('Al'''_2Ho_4O_2)''$,(2 or 4)$OH_2$.

Collyrite, ... $SiHo_2('Al'''_2Ho_5O)_2,4OH_2$.

Porcelain clay of Passau, . . .
$$\begin{array}{l} SiHo_2 \\ SiHo_2 \end{array} ('Al'''_2Ho_2O_4)^{iv}.$$

Kaolin (*porcelain clay, china clay*),
$$\left\{\begin{array}{l} SiHo \\ O \\ SiHo \end{array}\right. ('Al'''_2Ho_2O_4)^{iv}.$$

Razoumoffskin, ...
$$\begin{array}{l} SiHo_2 \\ SiHo_2('Al'''_2O_6)^{vi}. \\ SiHo_2 \end{array}$$

Wörthite, ...
$$\begin{array}{l} Si \\ SiO \\ Si \end{array} \begin{array}{l} ('Al'''_2HoO_5)^{v}. \\ ('Al'''_2HoO_5)^{v} \end{array}$$

Cimolite (*kaolin of Ellenbogen*), .
$$\begin{array}{l} SiHo_3 \\ SiO- \\ SiO- \\ SiHo_3 \end{array} ('Al'''_2O_6)^{vi}.$$

Agalmatolite, ...
$$\begin{array}{l} SiOHo \\ SiO- \\ SiO- \\ SiOHo \end{array} ('Al'''_2O_6)^{vi}.$$

Malthacite, ... $Si_8O_{11}Ho_4('Al'''_2O_6)^{vi}$.

Analcime, ...
$$\begin{array}{l} \left\{\begin{array}{l} SiHo_2Nao \\ O \\ Si \end{array}\right. \\ \left\{\begin{array}{l} Si \\ O \\ SiHo_2Nao \end{array}\right. \end{array} ('Al'''_2O_6)^{vi}.$$

Albite, ...
$$\begin{array}{l} SiONao- \\ \left\{\begin{array}{l} SiO- \\ O \\ SiO- \end{array}\right. \\ \left\{\begin{array}{l} SiO- \\ O \\ SiO- \end{array}\right. \\ SiONa- \end{array} ('Al'''_2O_6)^{vi}.$$

Lepidolite, ... $Si_9O_8Ko_2Lio_4('Al'''_2O_6)^{vi}{}_2('Al'''_2F_4O_2)''$.

Petalite, ... $Si_{30}O_{45}Nao_2Lio_4('Al'''_2O_6)^{vi}{}_4$.

Spodumene, ... $\mathbf{Si}_{15}O_{15}Lio_6('Al'''_2O_6)^{vi}_4$.

Wernerite, ... $\mathbf{Si}_2Cao''('Al'''_2O_6)^{vi}$.

Prehnite, ... $\mathbf{Si}_3Ho_2Cao''_2('Al'''_2O_6)^{vi}$.

Zoisite, ... $\mathbf{Si}_4Cao''_3\left(\left\{\begin{matrix}'Al'''_2O_5\\ O\\ 'Al'''_2O_5\end{matrix}\right\}\right)^{x}$.

Saponite, ... $\mathbf{Si}_7(Mgo''_6Ho_{10}('Al'''_2O_6)^{vi}$.

Topaz, ... $\mathbf{Si}_3('Al'''_2O_5F)^{v}('Al'''_2O_4F_2)^{iv}('Al'''_2O_4F)'''$.

(See also Silicates, p. 319.)

Ultramarine.

Various native double silicates of aluminium with other metals contain sulphur as an essential constituent. One of these, a double silicate and sulphide of aluminium and sodium, forms the mineral *lapis lazuli*, prized for its splendid blue color, and employed as a material for vases and inlaid or mosaic work. It is sometimes found crystallized in dodecahedra, but generally occurs massive. It has not as yet been found possible to express the composition of this mineral by means of a formula. The powdered mineral was formerly employed as a valuable blue pigment under the name of *ultramarine*, a substance which is now prepared artificially. For this purpose china clay (*infra*) is heated in crucibles along with sodic sulphate and charcoal. The sodic sulphate is reduced to sodic sulphide, which then combines with the aluminic silicate. The product is a white mass, which, however, speedily becomes green. This substance, known as *green ultramarine*, is also employed as a pigment. When green ultramarine is heated with sulphur, allowing the sulphur to burn off in air, it assumes a blue color, and is thus converted into the ordinary blue ultramarine of commerce. The same change is effected when green ultramarine is heated with ammonic chloride, or when chlorine is passed over it, but the sulphur method is employed in practice. No difference in chemical composition can be detected between the green and the blue modification. When ultramarine is treated with hydrochloric acid, it is decolorized with evolution of sulphuretted hydrogen and separation of amorphous silicic acid. It is used in paper-staining, in calico-printing, and as an oil paint.

Porcelain and Pottery.

Porcelain and pottery in all their forms are manufactured primarily from clay, an aluminic silicate. This material possesses sufficient plasticity to allow of its being moulded into any desired form, whilst by the action of heat it is rendered sufficiently hard and tenacious to resist the wear of every-day use. The purest clay is *kaolin* or *china clay*, $\left\{\begin{matrix}\mathbf{Si}Ho\\ O\\ \mathbf{Si}Ho\end{matrix}\right.('Al'''_2Ho_2O_4)^{iv}$, which is formed from felspar, $\mathbf{Si}_6O_8Ko_2('Al'''_2O_6)^{vi}$, by weathering, the grad-

ual action of water removing the potash together with a portion of the silicic acid, and leaving an aluminic silicate. Kaolin sometimes occurs in six-sided tablets, but generally forms a white or yellowish-white mass. The commoner clays consist of kaolin with various impurities —calcic and magnesic carbonates, ferric oxide, sand, and organic matter. Kaolin does not fuse when heated, but bakes together into a hard porous mass; in order, therefore, to increase the durability of utensils manufactured from it, the kaolin is mixed with some fusible material, technically known as a *frit*, which by its fusion binds the whole together. The materials added are ground feldspar, quartz-sand, chalk, gypsum, bone-ash, and sodic or potassic carbonate—the nature of the frit varying with the quality of the ware required. The materials are carefully ground under water and mixed. The mixing is an operation of great nicety, inasmuch as it is necessary to preserve the same composition of the mixture for a given kind of ware; and as the composition of the clay is apt to vary, this constancy of composition can only be attained by suitably varying the proportions of the other ingredients: thus, if the clay should happen to contain a larger quantity of silicia, less quartz-sand will have to be added, and so on. The presence of organic matter is objectionable, as organic substances disengage gas during the firing, and are thus liable to spoil the work. By allowing the mixture to stand in a moist state for a considerable length of time, the organic matter undergoes putrefaction, and is thus got rid of. The plastic mass is then moulded into the required form, either on the potter's wheel, or by means of moulds. The articles are then allowed to dry at ordinary temperatures, and are then in some cases subjected to a preliminary process of firing at a relatively low temperature, known as *baking*, after which they are glazed. The glaze is of various kinds, according to the nature and quality of the ware; but in every case it consists of some material which in the subsequent firing fuses, and imparts to the porous ware a smooth vitreous surface, impermeable to liquids. The glaze is generally employed in the form of a fine powder, which is either suspended in water, into which the baked articles are dipped, or is dusted upon their surface. Another mode of glazing consists in volatilizing in the porcelain kiln some material which is thus deposited on the surface of the articles, and forms with the silica which they contain a fusible glaze (salt-glazing). The finer sorts of porcelain and earthenware are not exposed to the direct action of the flame in firing, but are inclosed in fire-clay crucibles, known as *saggers*, by which means they are protected from the action of the smoke and ash. The porcelain kiln consists of a tall reverberatory furnace, divided usually into three stories or floors, through which the flame passes. The upper story is employed for baking, the two lower for firing. The firing is continued during eighteen hours, after which the kiln is allowed to cool slowly for three or four days in order to anneal the ware.

Porcelain or China.—This is the finest description of ware. It was manufactured in China before the Christian era; but the art of making true porcelain was not discovered in Europe till the commencement of the 18th century. There are two chief classes of porcelain: *hard porcelain*, to which class the Chinese, German and Sèvres porcelain belong;

and *tender porcelain*, produced especially in England. Great care has to be exercised in the selection of the materials in order that the resulting porcelain may be colorless. The presence of ferric oxide and organic matter is to be avoided. The purest kaolin forms the basis of all porcelain; and upon the nature of the frit the difference in properties of the various kinds of porcelain depends. In the case of hard porcelain, the frit consists of calcic and potassic silicates: thus the paste employed at Sèvres for ornamental porcelain has the composition: Washed kaolin, 62 parts; chalk, 4; quartz-sand, 17; felspar, 17. The glaze for this porcelain consists of a mixture of felspar and quartz. In the case of English porcelain, a frit consisting of bone-ash or a mineral phosphate, together with borax, is employed. This frit is much more fusible than the preceding, and the porcelain thus obtained is softer. This porcelain is glazed with an easily fusible mixture of bone-ash, plumbic oxide, potashes, sand, and borax. Tender porcelain must be baked before applying the glaze, and then fired; hard porcelain is sometimes glazed after drying at ordinary temperatures. The reason for this difference in treatment is to be found in the fact that in the case of tender porcelain the glaze is very much more fusible than the mass, whilst with hard porcelain this is not the case.

Porcelain forms a white, translucent, homogeneous mass. Hard porcelain resists sudden changes of temperature and the action of acids and alkalies much better than glass, and is for this reason employed in the manufacture of laboratory vessels.

Stoneware differs from porcelain in being always opaque and generally more or less colored. The materials employed are not so pure, and generally contain ferric oxide. It is more fusible than porcelain. In order to glaze this ware, the process known as salt-glazing is employed. The articles to be glazed are dipped in sand and water, and then gradually heated to a very high temperature in the kiln. A quantity of common salt is then thrown into the kiln. The salt volatilizes, forming with the sand a fusible sodic silicate, which combines with the other silicates present to yield a glass or glaze, and coats the ware, rendering it impervious to water. The explanation of the process is as follows: Silicic anhydride alone is not capable of decomposing sodic chloride at any temperature; but when the two substances are strongly heated together in presence of the vapor of water, hydrochloric acid is expelled and sodic silicate formed:

$$\underset{\text{Silicic anhydride.}}{\mathbf{Si}O_2} + \underset{\text{Sodic chloride.}}{2NaCl} + \underset{\text{Water.}}{\mathbf{O}H_2} = \underset{\text{Sodic silicate.}}{\mathbf{Si}ONao_2} + \underset{\text{Hydrochloric acid.}}{2HCl.}$$

The water is furnished by the combustion of the fuel. At the same time another portion of sodic chloride acts upon the ferric silicate contained in the clay, yielding sodic silicate and volatile ferric chloride:

$$\underset{\text{Ferric silicate.}}{\mathbf{Si}_3O_3('Fe'''_2O_6)^{vi}} + \underset{\text{Sodic chloride.}}{6NaCl} = \underset{\text{Sodic silicate.}}{3\mathbf{Si}ONao_2} + \underset{\text{Ferric chloride.}}{\mathbf{Fe}_2Cl_6.}$$

The iron present on the outer surface of the ware is thus removed.

Earthenware.—This ware differs from the two preceding varieties, inasmuch as no fusion or vitrification occurs during firing, and the body of the ware remains porous. A piece of unglazed earthenware adheres to the tongue. In the manufacture of fine earthenware a paste is employed consisting of a mixture of fine plastic clay and ground flints. This mass burns white on firing, and is afterwards glazed with an opaque lead glaze. Common earthenware is prepared from inferior clay.

In the manufacture of *common pottery ware*—bricks, flower-pots, etc. —impure clays are employed. The color, red or yellow, is due to the presence of ferric and other oxides in the clay.

Fire-bricks, melting crucibles, and other articles which are required to resist a high temperature, are prepared from a pure clay rich in silica. In order to lessen the shrinkage which this clay suffers in firing, a quantity of finely powdered burnt clay (broken pots of the same material) is added.

COMPOUND OF ALUMINIUM WITH SULPHUR.

Aluminic sulphide, $Al_2S''_3$, is formed as a black mass, which acquires metallic lustre under the burnisher, by the union of aluminium with sulphur at a red heat, and may also be obtained as a white vitreous substance by passing the vapor of carbonic disulphide over alumina heated to whiteness:

$$\underset{\text{Aluminic oxide.}}{2Al_2O_3} + \underset{\text{Carbonic disulphide.}}{3CS''_2} = \underset{\text{Aluminic sulphide.}}{2Al_2S''_3} + \underset{\text{Carbonic anhydride.}}{3CO_2.}$$

Water decomposes it, yielding aluminic hydrate and sulphuretted hydrogen.—Alkaline sulphides and sulphhydrates precipitate aluminic hydrate from solutions of aluminium salts.

General Properties and Reactions of the Compounds of Aluminium.—The salts of aluminium with colorless acids are colorless. They have a sweet but very astringent taste. Their solutions redden blue litmus. *Caustic alkalies*, *ammonia*, *ammonic carbonate*, *baric carbonate*, and *ammonic sulphide*, all precipitate aluminic hydrate—in the case of the carbonates with evolution of carbonic anhydride, and in the case of ammonic sulphide with evolution of sulphuretted hydrogen. The precipitate is readily soluble in caustic alkalies, only very sparingly soluble in ammonia. If aluminium compounds be ignited before the blowpipe, then moistened with cobaltous nitrate and again ignited, a pale blue mass (Thenard's blue) is obtained. Aluminium compounds do not color the non-luminous flame. The spark-spectrum of aluminium is very complex.

GALLIUM, Ga.

Atomic weight = 68.8. *Molecular weight unknown. Sp. gr.* 5.9. *Fuses at* 30.1° C. (86.2° F.). *Atomicity* ^{iv}, *but is always a pseudo-triad. Evidence of atomicity: analogy with aluminium.*

History.—Gallium was discovered in 1875 by Lecoq de Boisbaudran with the aid of the spectroscope.

Occurrence.—Gallium is one of the rarest elements. It occurs in minute traces in the zinc blende from Pierrefitte in the Pyrenees, from Austria and from Bensberg. The blende from the latter source, which is the richest in gallium, contains only 0.0016 per cent. of this metal.

Extraction.—The zinc ores containing gallium are dissolved in acid—hydrochloric acid, sulphuric acid, or aqua-regia, according to the nature of the ore—and the solution is partially precipitated with metallic zinc. The gallium, along with the other foreign metals originally contained in the zinc ore, is precipitated upon the zinc. The precipitate is redissolved in hydrochloric acid and the solution again treated with metallic zinc. This precipitate is again dissolved in hydrochloric acid, and sulphuretted hydrogen is passed into the solution. The liquid is filtered from sulphides, and, after expelling the sulphuretted hydrogen by boiling, fractionally precipitated with sodic carbonate as long as spectroscopic examination shows the presence of gallium in the fractions. The various fractions are dissolved in sulphuric acid, the solution evaporated to dryness, and the residue heated so as to expel the excess of acid. On treating with hot water, basic gallic sulphate separates, and must be filtered off hot. The basic sulphate is dissolved in the smallest possible quantity of sulphuric acid, and, after adding ammonic acetate, the gallium is precipitated from the solution as sulphide by means of sulphuretted hydrogen. In order to obtain metallic gallium the sulphide is again dissolved in sulphuric acid and, after adding an excess of caustic potash, in which the gallic hydrate is soluble, the liquid is subjected to electrolysis, employing electrodes of platinum. The electrolytically deposited gallium is washed with dilute nitric acid, and is then pure.

Properties.—Gallium is a bluish-white metal of sp. gr. 5.9. It fuses at the low temperature of 30.1° C. (86.2° F.), and remains for a long time in a state of superfusion, even at 0° C., but when touched with a piece of the solid metal instantly solidifies in pyramidal crystals. The metal when fused is silver-white and more lustrous than in the solid state. It dissolves with evolution of hydrogen in hydrochloric acid and in caustic potash. Nitric acid is almost without action upon it in the cold, but dissolves it on heating. When a solution of gallic chloride is warmed with metallic zinc, gallic oxide or a basic salt is precipitated.

COMPOUNDS OF GALLIUM.

Gallic chloride, $'\mathbf{Ga}'''_2Cl_6$, forms soluble, deliquescent, colorless needles. Excess of water decomposes it with separation of an oxy-chloride.

Gallic oxide, $'\mathbf{Ga}'''_2O_3$, is a white precipitate insoluble in water, but soluble in caustic alkalies and in ammonia.

Gallic sulphate, $\left.\begin{array}{l}\mathbf{S}O_2 \\ \mathbf{S}O_2 \\ \mathbf{S}O_2\end{array}\right] ('Ga'''_2O_6)^{vi}$, is very soluble. From mixed solutions of this salt with ammonic sulphate, regular crystals of *ammonium gallium alum*, $\left.\begin{array}{l}\mathbf{S}O_2Amo \\ \mathbf{S}O_2 \\ \mathbf{S}O_2 \\ \mathbf{S}O_2Amo\end{array}\right] ('Ga'''_2O_6)^{vi}, 24\mathbf{O}H_2$, are deposited.

General Properties and Reactions of the Compounds of Gallium.—Gallium is most readily recognized by means of its spark

spectrum, which consists of two lines in the violet. The flame spectrum shows only one of these lines, and that but faintly. The other characteristic properties of the gallium compounds are given above.

CHAPTER XXXVII.

METALS OF THE RARE EARTHS.

The metals of this group occur, generally together, in a few rare minerals. Their separation is a matter of extreme difficulty owing to the similarity of their compounds. Indeed it is doubtful in the case of most of them whether pure compounds have ever been obtained—a fact pointed to by the discrepant results arrived at by careful experimenters in the determination of the atomic weights of these elements. The most important metals of this group are cerium, lanthanum, didymium, yttrium, and erbium.

TETRAD ELEMENTS.

Section III.

CERIUM, Ce.

Atomic weight = 140.5. *Molecular weight unknown. Sp. gr.* 6.728. *Atomicity* ^{iv}, *also a pseudo-triad. Evidence of atomicity:*

$$\text{Cerous chloride,} \quad \ldots\ldots \quad \left\{\begin{array}{l} \mathbf{Ce}'''Cl_3 \\ \mathbf{Ce}'''Cl_3. \end{array}\right.$$

$$\text{Ceric oxide,} \quad \ldots\ldots \quad \mathbf{Ce}^{iv}O_2.$$

History.—Ceria was discovered by Klaproth in 1803, but was first recognized as the oxide of a new metal by Berzelius and Hisinger.

Occurrence.—Cerium always occurs together with lanthanum and didymium. The most abundant source of these three metals is the mineral *cerite*, in which they occur as silicates. They also occur in *monazite* as phosphates, and in *fluocerite* as *fluorides.*

Preparation.—Separation of Cerium, Lanthanum, and Didymium.—Finely powdered cerite is mixed with concentrated sulphuric acid so as to form a thick cream, and the mixture is heated in a Hessian crucible—first gently in order to expel the acid, finally to low redness. The cooled contents of the crucible are powdered and added in small portions at a time to water at 0° C., great care being taken to avoid any rise of temperature. The solution, after filtering from sand and other insoluble matters, is treated with sulphuretted hydrogen in order to precipitate copper, bismuth, molybdenum, and lead. After removing these, chlorine is passed in to reoxidize the iron and, after acidifying with

hydrochloric acid, oxalic acid is added in excess. In this way the cerium, lanthanum, and didymium—together with any yttrium and erbium, if present—are precipitated as oxalates. The precipitate is strongly ignited, by which means the oxalates are converted into oxides. These are dissolved in nitric acid and the solution evaporated to a syrup. The syrupy solution is then diluted with water and poured into a large excess of boiling water containing 2 c.c. of sulphuric acid to the litre. The cerium is thus precipitated as a basic ceric sulphate. This precipitate is dissolved in sulphuric acid and re-precipitated as basic sulphate by again pouring into boiling water, repeating these operations until the solution of the cerium salt in sulphuric acid no longer shows the absorption spectrum of didymium. The cerium compound may then be regarded as pure.

In order to obtain the lanthanum and didymium from the filtrate from the first precipitation of basic ceric sulphate, this liquid is first boiled with pulverized magnesite, which precipitates the rest of the cerium as oxide, whilst the lanthanum and didymium remain in solution. The lanthanum and didymium are then precipitated by the addition of oxalic acid to the solution acidified with hydrochloric acid, the oxalates are converted as above into oxides, these are dissolved in sulphuric acid, the solution is evaporated to dryness, and the salt heated to low redness. The anhydrous sulphates thus obtained are dissolved in five times their weight of ice-cold water, adding the salt to the water in small quantities at a time, and never allowing the temperature to rise above 5° C. (41° F.). On warming the solution, the greater part of the lanthanum separates out as a sulphate of the formula $\mathbf{S}_3O_6Lao'''_2,9\mathbf{O}H_2$, carrying down with it, however, a small quantity of didymium. This precipitate is filtered off hot, employing a hot-water funnel; the solution is reserved for the preparation of a pure didymium compound. In order to free the precipitate of lanthanous sulphate from didymium, it is necessary to repeat the operations of dehydrating at low redness, dissolving in ice-cold water and precipitating by warming the solution, until the solution no longer shows the spectrum of didymium. For this purpose from six to eight repetitions of this series of operations are generally necessary.

In order to obtain a pure didymium salt the mother liquor from the first precipitation of the lanthanous sulphate is fractionally precipitated with oxalic acid. When the oxalic acid is very gradually added, the precipitate which is at first formed redissolves; but at length a point is reached when a permanent precipitate of crystalline, pink-colored didymous oxalate separates out. This oxalate is converted into oxide, then into sulphate, which is fractionally precipitated in the same way. After several repetitions of this treatment a product is obtained, from the spark-spectrum of which the lanthanum lines are absent.

The metals were originally prepared by heating the chloride with sodium. They may, however, be obtained more readily and in a state of greater purity by the electrolysis of the fused chlorides.

Properties.—Metallic cerium possesses the color and lustre of iron. It is malleable and ductile. It tarnishes in moist air. Its fusing-point lies between those of antimony and silver. When heated in air it burns

even more brilliantly than magnesium. It slowly decomposes cold water. Dilute sulphuric and hydrochloric acids rapidly dissolve it with evolution of hydrogen; but cold concentrated sulphuric acid and concentrated nitric acid are without action upon it.

COMPOUNDS OF CERIUM.

Cerous chloride, $'Ce'''_2Cl_6$.—Finely-divided metallic cerium inflames when thrown into chlorine, yielding a yellowish-white deliquescent mass of cerous chloride. This compound is also formed when chlorine is passed over a strongly heated mixture of cerous oxide and carbon. When a solution of the oxide in hydrochloric acid is evaporated over sulphuric acid, an aquate of the formula $'Ce'''_2Cl_6,5OH_2$ is obtained in crystals. On heating, this salt is decomposed with formation of an oxychloride, but by the addition of ammonic chloride this decomposition may be prevented and the anhydrous chloride obtained.

The *bromide* and *iodide* have also been prepared.

Cerous fluoride, $'Ce'''_2F_6$, is a white precipitate.—*Ceric fluoride*, CeF_4,OH_2, is a brownish powder obtained by the action of hydrofluoric acid upon ceric hydrate. When cautiously heated it first loses water and a part of its fluorine as hydrofluoric acid; on heating more strongly, a gas is given off which smells like chlorine and liberates iodine from a solution of potassic iodide—probably free fluorine (Brauner).

Cerous oxide, $'Ce'''_2O_3$, is formed when the oxalate, or the carbonate, or ceric oxide, is heated in a current of hydrogen. It is a bluish-green powder, which absorbs oxygen from the air, and is converted into ceric oxide.—*Cerous hydrate* is thrown down as a bulky white precipitate when a caustic alkali is added to the solution of a cerous salt. Exposure to the air colors it yellow, owing to oxidation.

Ceric oxide, CeO_2, is obtained by heating the oxalate or the nitrate in air or oxygen. Thus prepared it forms a colorless or faint-yellow powder, but by heating cerous chloride with borax in a wind furnace for forty-eight hours, it may be obtained in crystals belonging to the regular system. On heating, it becomes darker in color, but resumes its original tint on cooling. Hydrochloric act dissolves it, yielding a yellow solution, which when warmed evolves chlorine, and then contains cerous chloride. With concentrated sulphuric acid it also yields a yellow solution, which possesses oxidizing properties and evolves ozonized oxygen.—The *hydrate* has the formula Ce_2OHo_6.

Cerous nitrate, $N_6O_{12}('Ce'''_2O_6)^{vi},12OH_2$, is best prepared by dissolving ceric oxide in nitric acid with the addition of alcohol, the latter substance acting as a reducing agent. It forms a crystalline mass.

Ceric nitrate, $N_4O_8Ceo^{iv}$, is formed when ceric oxide is dissolved in concentrated nitric acid. It is soluble in strongly acid solutions, but excess of water decomposes it with separation of a basic salt. It forms double salts with other nitrates.

Cerous sulphate, $S_3O_6('Ce'''_2O_6)^{vi},9OH_2$, is deposited in large octahedra or prisms when a solution of ceric oxide in sulphuric acid is mixed with alcohol or sulphurous acid and allowed to evaporate spontaneously. Hot solutions deposit the anhydrous salt in minute crystals, which are

soluble in six parts of cold and sixty parts of boiling water.—*Cerous potassic sulphate*, $\mathbf{S}_6O_{12}Ko_6('Ce'''_2O_6)^{vi}$, separates as a white crystalline powder when an excess of potassic sulphate is added to a solution of the preceding salt. It is sparingly soluble in water, and almost insoluble in a concentrated solution of potassic sulphate. Cerous sulphate forms similar double salts with the sulphates of sodium and ammonium.

Ceric sulphate, $\mathbf{S}_2O_4Ceo^{iv},7\mathbf{O}H_2$, is a yellow crystalline mass.

Cerous phosphate, $\mathbf{P}_2O_2('Ce'''_2O_6)^{vi}$, occurs as *monazite*. A portion of the cerium in this mineral is isomorphously replaced by lanthanum and didymium.

PENTAD ELEMENTS.

Section II.

DIDYMIUM, Di.

Atomic weight = 146. *Molecular weight unknown.* *Sp. gr.* = 6.544. *Atomicity* ''' *and* v.

History.—Didymium was discovered by Mosander in 1841.

Occurrence and Preparation.—See Cerium, p. 578.

Properties.—In its properties didymium resembles the two foregoing metals, except that it has a slightly yellow tint.

COMPOUNDS OF DIDYMIUM.

Didymous chloride, $\mathbf{Di}Cl_3$, is a rose-colored crystalline mass. Its solutions deposit rose-red crystals with 6 aq.

Didymous oxide, $\mathbf{Di}_2O_3$, is prepared by igniting the oxalate or the hydrate. It forms a white or bluish powder, neither fusible nor volatile, which when strongly ignited gives a continuous spectrum intersected by bright bands, corresponding in position with the dark bands of the absorption spectrum of the didymium salts (cf. Erbia, p. 584).—*Didymous hydrate*, $\mathbf{Di}Ho_3$, is obtained as a pale pink-colored precipitate by adding a caustic alkali or ammonia to the solution of a didymous salt.

Didymic oxide, $\mathbf{Di}_2O_5$, is obtained as a chocolate-colored mass by heating the basic nitrate of didymium to dull redness in a current of oxygen.

Didymous nitrate, $\mathbf{N}_3O_6Dio''',6\mathbf{O}H_2$, forms large rose-red deliquescent crystals.

Didymous sulphate, $\mathbf{S}_3O_6Dio'''_2,8\mathbf{O}H_2$, crystallizes in soluble, rose-red monoclinic prisms.

TRIAD ELEMENTS.*

SECTION IV.

LANTHANUM, La.

Atomic weight = 138.5. *Molecular weight unknown. Sp. gr.* 6.163. *Atomicity* ''' ?

History.—Lanthanum was discovered by Mosander in 1839.

Occurrence and Preparation.—See Cerium, p. 578.

Properties.—Lanthanum is a malleable metal of an iron-gray color. The freshly cut surface is very lustrous, but speedily tarnishes on exposure to air. In its behavior towards water and acids it resembles cerium, except that it is attacked in the cold both by concentrated and by dilute nitric acid.

COMPOUNDS OF LANTHANUM.

Lanthanous chloride, $\mathbf{La}Cl_3$, is prepared like cerous chloride, which it resembles in its properties.

Lanthanous oxide, $\mathbf{La}_2O_3$, is obtained as a white powder by heating the oxalate or the nitrate. It combines with water with evolution of heat, and is converted into the hydrate $\mathbf{La}Ho_3$.

Lanthanous nitrate, $\mathbf{N}_3O_6Lao''',6\mathbf{O}H_2$, forms colorless, deliquescent, tabular crystals.

Lathanous sulphate, $\mathbf{S}_3O_6Lao''_2,9\mathbf{O}H_2$, crystallizes in six-sided prisms. The anhydrous salt is readily soluble in ice-cold water, but on gently warming the solution the above aquate separates in microscopic star-shaped crystals, which at 13° C. dissolve in less than 6 parts of water, but at 100° C. require 115 parts for their solution. (See Separation of Lanthanum, p. 579.)

YTTRIUM, Y.

Atomic weight = 89.8. *Molecular weight unknown. Atomicity* ''' ?

History.—The earth yttria was discovered by Gadolin in 1794.

Occurrence.—This element occurs, always accompanied by erbium, in a few very rare minerals: thus as silicate in *gadolinite* and *orthite* (along with cerium, lanthanum, didymium, beryllium, iron, and other metals); also as tantalate, niobate, and phosphate. Recently, however, the spectroscope has shown yttrium to be a very widely diffused element (Crookes).

* The remaining elements of this group have been classed as triadic; but it is quite possible that they may be only pseudo-triadic.

Preparation. Separation of Yttrium and Erbium.—Gadolinite is decomposed with hydrochloric acid and evaporated to expel the excess of acid. The residue is extracted with dilute hydrochloric acid, and the solution is heated to boiling and precipitated with oxalic acid. The precipitate, which contains, in the form of oxalates, all the yttrium and erbium, along with calcium, cerium, lanthanum, didymium, and traces of manganese and silica, is washed by decantation and heated in an open platinum dish, until the oxalic acid is totally destroyed. The mixed oxides thus obtained are dissolved in nitric acid, and a concentrated solution of potassic sulphate is added, which precipitates the cerium, lanthanum, and didymium as double sulphates of these metals with potassium. From the filtrate the yttrium and erbium are again precipitated as oxalates, the oxalates converted by heating into oxides, the latter redissolved in nitric acid, and the solution examined with the spectroscope for didymium, the presence of which metal can be readily detected by its characteristic absorption spectrum. If didymium is present, the precipitation with potassic sulphate and the other operations must be repeated until a solution is obtained which does not give the didymium spectrum. A trace of calcium is got rid of by precipitating the yttrium and erbium as hydrates by ammonia. In order to separate the yttrium and erbium, the pure hydrates are dissolved in nitric acid, and the mixed nitrates are carefully heated in a platinum dish over a small flame until the first bubbles of nitrous anhydride begin to make their appearance. The moment this point is reached, the dish is rapidly cooled in order to prevent further decomposition, and the residue is dissolved in a quantity of warm water just sufficient to prevent the solution from becoming turbid on boiling. This solution deposits on cooling needles of a basic nitrate of erbium, which is, however, still contaminated with yttrium. Further crops of this salt, but still less pure, are obtained from the mother liquors. The purer crops are mixed, dissolved in nitric acid, again heated to incipient decomposition, and treated as above, repeating this operation until a pure erbium salt is obtained. In order to separate the yttrium in a state of purity from the erbium, with which it remains mixed in the mother liquors in the form of nitrate, the solution is evaporated to dryness, the residue heated to redness, and, after cooling, extracted with water; the solution thus obtained is again evaporated to dryness, heated, and the residue extracted with water, repeating these operations until a solution is obtained which no longer gives an absorption spectrum of erbium. From this solution, which contains a basic yttric nitrate, the yttrium is precipitated by oxalic acid. The pure oxalate of yttrium is converted by ignition into the oxide.

Properties.—Pure metallic yttrium and erbium have not been prepared. By heating the mixed chlorides of the two metals with sodium, a black powder has been obtained, which assumes a metallic lustre under the burnisher. This metallic substance burns brilliantly when heated in air. Water decomposes it slowly at ordinary temperatures, more rapidly on boiling. Acids dissolve it readily, with evolution of hydrogen.

The attempt to prepare yttrium and erbium by the electrolytic decomposition of the chlorides has not proved successful.

COMPOUNDS OF YTTRIUM.

Yttrous chloride, YCl_3.—When the above described impure yttrium is heated in chlorine, it is converted into a non-volatile chloride. By dissolving the oxide in hydrochloric acid and evaporating, an aquate of the formula $YCl_3,6OH_2$ is obtained, which when heated evolves hydrochloric acid. By heating the aquate with ammonic chloride anhydrous yttrous chloride may be obtained.

The *bromide* and *iodide* closely resemble the chloride.

Yttrous fluoride occurs in combination with the fluorides of cerium and calcium in the mindral *yttrocerite.*

Yttrous oxide (*Yttria*), Y_2O_3, is obtained as a yellowish-white powder by igniting the oxalate (see p. 583). It is neither fusible nor volatile. When strongly heated it emits a pure white light, which when examined by means of the spectroscope, gives a perfectly continuous spectrum, without any trace of lines or bands, a behavior which affords a means of distinguishing this oxide from that of erbium. Water neither dissolves it nor converts it into hydrate. Mineral acids slowly dissolve it, yielding salts.—*Yttrous hydrate*, YHo_3, is obtained as a gelatinous precipitate when alkalies are added to solutions of yttrium salts.

Yttrous nitrate, $N_3O_6Yo''',6OH_2$, is readily soluble, and forms long needles permanent in air. A basic nitrate of the formula $N_3O_6Yo''',YHo_3,3OH_2$, is obtained by heating the normal nitrate to incipient decomposition and crystallizing from a small quantity of water.

Yttrous sulphate, $S_3O_6Yo'''_2,8OH_2$, is deposited from its solutions in well-formed crystals, which become anhydrous only at a high temperature. The anhydrous salt is much more soluble than the crystallized aquate. A saturated solution of the anhydrous salt prepared at 15° C. (59° F.) deposits a portion of the salt in the hydrated state on warming.

ERBIUM, Er.

Atomic weight = 165.9. *Molecular weight unknown.* *Atomicity* '''.

History.—Erbium was discovered in 1843 by Mosander.

Occurrence, Preparation, and Properties.—See Yttrium, p. 583.

COMPOUNDS OF ERBIUM.

These resemble the compounds of yttrium.

Erbous oxide (*Erbia*), Er_2O_3, is obtained by igniting the oxalate or nitrate. It forms an amorphous mass of a yellowish color. It does not fuse at the highest temperatures, but, when strongly heated, emits a greenish light, which, when examined spectroscopically, gives a continuous spectrum, intersected however by bright bands, the position of which agrees with that of the dark bands in the absorption spectrum of the solutions of erbium salts. Towards acids erbia behaves like

yttria.—*Erbous hydrate*, $\mathbf{Er}Ho_3$, is precipitated by alkalies from the solutions of the salts of erbium.

Erbous nitrate.—A basic nitrate of the formula $\mathbf{N}_3O_6Ero''',\mathbf{Er}Ho_3.3\mathbf{O}H_2$, obtained like the corresponding yttrium salt, is employed in the separation of erbium from yttrium.

Erbous sulphate, $\mathbf{S}_3O_6Ero'''_2,8\mathbf{O}H_2$, is deposited from its solutions at 100° C. in well-formed crystals. It closely resembles in its properties yttrous sulphate.

All the salts of erbium when in solution display a spectrum with characteristic absorption bands.

TERBIUM, Tr.

Atomic weight = 148.8 (?).

Very little is known concerning this element, which occurs along with yttrium and erbium in samarskite. The metal has not been isolated, and even its compounds have not been obtained free from erbium. The above atomic weight is therefore to be regarded only as an approximation.

Another metal, *ytterbium* (*atomic weight* = 172.8) has lately been added by Marignac to the list of the metals of the rare earths. It occurs in crude erbia. Its oxide is white and gives no absorption spectrum.

SCANDIUM, Sc (*atomic weight* = 44).—Very little is yet known concerning this rare element, which was discovered by Nilson in 1879. The metal has not yet been isolated. It occurs along with the other rare earths in gadolinite and euxenite. It is separated by means of the property which its nitrate possesses of undergoing decomposition at a relatively low temperature.

Scandous oxide, $\mathbf{Sc}_2O_3$, is a white infusible powder. Its salts closely resemble those of the other metals of this group.

SAMARIUM, Sm (*atomic weight* = 150), was discovered by Lecoq de Boisbaudran in samarskite. It is easily recognizable by means of its characteristic spectrum. The compounds of this element resemble those of didymium. *Samarous chloride*, $\mathbf{Sm}Cl_3,6\mathbf{O}H_2$, forms large tabular deliquescent crystals. *Samarous oxide*, $\mathbf{Sm}_2O_3$, is a white or faint-yellow powder. The solutions of its salts have a deep yellow color.

DECIPIUM, Dp (*atomic weight* = 159 ?) was discovered by Delafontaine in the samarskite of North Carolina. It has not yet been found possible completely to separate its compounds from those of didymium. The solutions exhibit a characteristic absorption spectrum.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF THE RARE EARTH METALS.—The corresponding compounds of these various metals are characterized by their great similarity, so that their separation is generally a matter of difficulty. The methods for the separation of the principal members of the group—yttrium, erbium, cerium, lanthanum, and didymium—have already been given (pp. 578 and 583).

CHAPTER XXXVIII.

TETRAD ELEMENTS.

Section IV.

PLATINUM, Pt.

Atomic weight = 194.4. *Molecular weight unknown.* *Sp. gr.* 21.5. *Fuses about* 2000° C. (3632° F.). *Atomicity* '' *and* iv. *Evidence of atomicity:*

Platinous chloride, ...	$Pt''Cl_2$.
Platinous oxide, ...	$Pt''O$.
Platinic chloride, ...	$Pt^{iv}Cl_4$.
Platinic oxide, ...	$Pt^{iv}O_2$.

History.—Platinum was first recognized as a distinct metal in the eighteenth century, though it was known as a refractory metallic substance a couple of centuries earlier.

Occurrence.—Platinum occurs only in the native state. Native platinum is never pure: it contains from 50 to 80 per cent. of platinum, the remainder consisting of iridium, palladium, rhodium, osmium, and ruthenium—which, together with platinum, constitute the so-called platinum metals—also gold, iron, and copper. This impure metal, or platinum "ore," usually forms minute grains, although larger masses or nuggets are also found. It occurs most frequently in the sand of rivers and in alluvial deposits. The chief localities from which platinum is obtained are the Urals, Borneo, California, Brazil, and Peru. Traces have been found in the auriferous sands of the Rhine. The supply from Russia is ten times as great as that from all the other parts of the world taken together, and amounts to about 800 cwt. yearly.

Extraction.—The following is the method employed at St. Petersburg in treating the platinum ore: The ore is first digested with dilute aqua-regia, which extracts the gold; then with concentrated aqua-regia, as long as anything dissolves. The insoluble portion consists of grains of a native alloy of osmium and iridium. The solution contains the platinum as platinic chloride, along with small quantities of other metals. Ammonic chloride is now added to the solution, and in this way the platinum is precipitated as ammonic platinic chloride ($PtCl_4,2NH_4Cl$) along with the small quantity of iridium which is present. The precipitate of ammonic platinic chloride is decomposed by heat, employing as low a temperature as possible, in order that the platinum may be obtained in a finely divided state. The metallic powder is formed into a cake by pressing it into a conical mould of brass, after which the cake is heated to whiteness, and welded into an ingot by hammering. In this form the platinum may be drawn into wire or rolled into plate, and otherwise worked like the most ductile metals. Instead of welding the platinum, Deville and Debray fuse the metal in a lime crucible by means of the oxy-coal-gas blowpipe.

Deville and Debray have also attempted to obtain platinum from its

ores in the dry way. For this purpose the ores are fused with galena, glass, and borax. The iron present in the ore is thus converted into sulphide. Litharge is then gradually added. The litharge and galena react to yield metallic lead, the sulphur burning off as sulphurous anhydride (see Lead, Extraction of). The platinum and the other metals contained in the ore, with the exception of osmiridium, dissolve in the lead. The liquid portion is ladled off from the osmiridium, cupelled, and the resulting platinum fused in a lime crucible as above described. This process has been abandoned, as the platinum obtained by it is not sufficiently pure.

Preparation of pure Platinum.—In order to obtain pure platinum, commercial platinum is dissolved in aqua-regia, and from the solution, after expelling the excess of acid, the platinum and iridium are precipitated by caustic soda as platinic hydrate (**Pt**Ho_4) and iridic hydrate (**Ir**Ho_4). A little alcohol is now added, and the liquid with the precipitate is boiled. Platinic hydrate is not altered by this treatment, but iridic hydrate is converted into a lower hydrate of the formula $\mathbf{Ir}_2Ho_6$, and on reacidifying with hydrochloric acid, these hydrates go into solution, yielding the corresponding chlorides. Di-iridic hexachloride is not precipitated by ammonic chloride, so that on adding to the liquid an excess of this reagent the whole of the platinum is thrown down in the form of pure ammonic platinic chloride, which, after washing, is converted by ignition into pure metallic platinum.

Properties.—Platinum is a white metal with a tinge of gray, capable of taking a high polish. When obtained by heating to redness compounds of platinum—for example, ammonic platinic chloride—it forms a loosely coherent gray mass, known as *spongy platinum.* In the very finely divided condition in which it is deposited from the solutions of its chloride by the action of reducing agents, it forms *platinum black*, a black powder, quite devoid of metallic lustre. Platinum is very malleable and ductile. Perfectly pure platinum has about the same hardness as copper, but the presence of a small quantity of iridium increases its hardness considerably. In the form of very thin wire it can be fused in the flame of a candle; * in larger masses it requires the heat of the oxyhydrogen flame for its fusion. The fusing-point has been estimated by Deville at 2000° C. (3632° F.). It does not combine directly with oxygen at any temperature, but possesses in the molten state the property of absorbing oxygen. The absorbed oxygen is expelled during the solidification of the metal, which thus exhibits the phenomenon of "spitting" (see Silver, p. 451). In like manner hydrogen passes through a diaphragm of red-hot platinum, owing to the property which the metal possesses of dissolving the gas. The red-hot metal is, however, impermeable to oxygen, nitrogen, carbonic anhydride, and other gases. Cold platinum has the power of condensing various gases, especially oxygen, upon its surface. This action is exhibited in a very high degree by platinum black, which, owing to its state of extremely fine subdivision and consequently increased surface, is capable of thus con-

* It is possible that the fusion in this case is due to the formation of a fusible carbide of platinum.

densing eight hundred times its volume of oxygen. To this property is due the so-called catalytic action of platinum in bringing about the combination of various gases. Thus platinum black, when introduced into a mixture of oxygen and hydrogen, determines the explosion of the mixture. Sulphurous anhydride and oxygen, when passed over platinum black, form sulphuric anhydride; hydrogen and iodine unite to yield hydriodic acid—the action in this and in the former case being aided by gently heating the finely divided metal. A heated spiral of platinum wire, when plunged into a mixture of ether vapor and air, or of alcohol vapor and air, continues to glow, and effects the oxidation of the organic substance. Indeed, the wire need only be warmed to 50° C. in order to glow when introduced into the vapor.—Platinum is not attacked by any single acid; but aqua-regia, or any other liquid in which chlorine is contained or is being evolved, dissolves it. It is oxidized by fusion with caustic alkalies or with nitre. Fused alkaline cyanides also attack it. It unites directly with silicon when heated with it, to form a brittle silicide; and with phosphorus and arsenic it yields fusible compounds. With many of the metals it forms fusible alloys. A knowledge of these facts is of importance in working with vessels of platinum: thus phosphates ought never to be heated with carbon or with filter-paper in a platinum crucible, and the heating of compounds of easily reducible metals in such vessels is to be avoided altogether. Platinum vessels ought never to be heated over a smoky flame, as, owing to the alternate formation and oxidation of a carbide of platinum, the metal becomes blistered and porous. Contact with burning charcoal is also to be avoided, as the platinum combines with the silicon reduced from the ash.—Platinum may be sublimed at a red heat in a current of chlorine, and may thus be obtained in crystals. The sublimation of the platinum is only apparent and depends in reality upon the formation and decomposition, in rapid succession, of a chloride of platinum.

Uses.—The high fusing-point of platinum, and its power of resisting chemical action, have caused it to be extensively employed in the manufacture of vessels for laboratory purposes. Thus platinum crucibles and evaporating basins, platinum foil and wire, are in constant requisition in the processes of chemical analysis. Large platinum stills are used for the concentration of sulphuric acid. The marked electronegative character of platinum renders it capable of forming, with electropositive metals, such as zinc, voltaic combinations of high electromotive force. Grove's battery is a combination of this description.

Platinum forms two series of compounds: *platinous* compounds, in which the metal is dyadic; and *platinic* compounds, in which it is tetradic.

COMPOUNDS OF PLATINUM WITH THE HALOGENS.

a. Platinous Compounds.

Platinous chloride, $PtCl_2$, is obtained by heating platinic chloride to 225–230° C. (437–446° F.). It forms a grayish-green powder, insolu-

ble in water, soluble in hot hydrochloric acid, yielding a reddish-brown solution. It unites with other metallic chlorides to form double salts: thus the compounds $PtCl_2,2KCl$ and $PtCl_2,2NH_4Cl$ are obtained in large red prisms by adding potassic and ammonic chloride to the solution of platinous chloride in hydrochloric acid, and evaporating the liquid.—When platinous chloride is heated in a current of carbonic oxide, the gas is absorbed with formation of the compounds $PtCl_2,CO$, $PtCl_2,2CO$, and $PtCl_2,3CO$. It also unites directly with ethylene ($''C_2H_4$) and other unsaturated hydrocarbons.

Platinous bromide, $PtBr_2$, is prepared by heating hydric platinic bromide to 200° C. It forms a brown mass.

Platinous iodide, PtI_2, is obtained as a black powder by warming platinous chloride with a concentrated solution of potassic iodide.

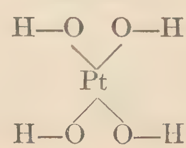
b. Platinic Compounds.

Platinic chloride, $PtCl_4$, is prepared by dissolving platinum in aqua-regia, destroying the nitric acid by repeated evaporation with hydrochloric acid, and heating to expel the excess of hydrochloric acid. It crystallizes from water in large red non-deliquescent crystals of the formula $PtCl_4,5OH_2$.—Platinic chloride forms numerous double salts with other chlorides: thus with hydrochloric acid it forms the compound $PtCl_4,2HCl$, which is deposited in brownish-red deliquescent prisms with 6 aq. from the solution of platinic chloride in hydrochloric acid. *Potassic platinic chloride*, $PtCl_4,2KCl$, and *ammonic platinic chloride*, $PtCl_4,2NH_4Cl$, are obtained as yellow crystalline precipitates, consisting of microscopic octahedra, when platinic chloride is added to solutions of potassic and ammonic chloride. These precipitates are almost insoluble in water and quite insoluble in alcohol. *Sodic platinic chloride* crystallizes in reddish-yellow prisms of the formula $PtCl_4.2NaCl,6OH_2$, readily soluble in water and in alcohol. The difference in the solubility of these compounds is turned to account in the separation of the alkali metals.

Platinic bromide, $PtBr_4$, has not been prepared, but *hydric platinic bromide*, $PtBr_4,2HBr,9OH_2$, is known.

Platinic iodide, PtI_4, separates as a black powder when potassic iodide is added to a solution of platinic chloride and the liquid warmed.

COMPOUNDS OF PLATINUM WITH OXYGEN AND HYDROXYL.

Platinous oxide, . .	PtO.	Pt=O.
Platinous hydrate, .	$PtHo_2$.	H—O—Pt—O—H.
Platinic oxide, . .	PtO_2.	O=Pt=O.
Platinic hydrate, . .	$PtHo_4$.	

Platinous oxide, **Pt**O.—This compound is obtained as a grayish-black powder by gently heating the corresponding hydrate.

Platinous hydrate, $\mathbf{Pt}Ho_2$, is a bulky black powder, obtained by digesting platinous chloride with warm caustic potash. Boiling caustic potash decomposes it with separation of metallic platinum and formation of platinic oxide. It acts as a weak base and yields with the hydracids the corresponding haloid salts; but the oxy-acids, with the exception of sulphurous acid, decompose it.

Platinic oxide, $\mathbf{Pt}O_2$, is a black powder obtained by gently heating platinic hydrate.

Platinic hydrate, $\mathbf{Pt}Ho_4$.—A solution of platinic chloride is precipitated by boiling with caustic potash, and the precipitate is treated with acetic acid to remove the potash, when a white compound of the formula $\mathbf{Pt}Ho_4,2\mathbf{O}H_2$ remains. This, on drying at 100° C., parts with 2 aq. and assumes an amber-brown color. Platinous hydrate acts both as a weak base and as a weak acid. The salts which it forms with bases are known as *platinates*. *Baric platinate* is a yellow powder of the formula $\mathbf{Pt}Ho_2Bao'',3\mathbf{O}H_2$.

OXY-SALTS OF PLATINUM.

Very few of the simple oxy-salts of platinum have been prepared, but various double salts are known.

Platinous sulphite is obtained as a gummy mass of unknown composition by evaporating the solution of platinous hydrate in sulphurous acid.—*Potassic platinous sulphite*, $\mathbf{S}OPto'',3\mathbf{S}OKo_2,2\mathbf{O}H_2$ crystallizes in readily soluble needles. *Sodic platinous sulphite*, $\mathbf{S}OPto'',3\mathbf{S}ONao,7\mathbf{O}H_2$, is a sparingly soluble crystalline precipitate.

Platinonitrites.—Platinum forms a series of remarkable compounds with the nitrites of other metals. These compounds do not behave like ordinary double salts; the platinum cannot be detected in their solutions by the ordinary reagents. They may be regarded as salts of *platinonitrous acid*, $H_2Pt(NO_2)_4$.—*Potassic platinonitrite*, $K_2Pt(NO_2)_4$, is deposited in small lustrous prismatic crystals when solutions of potassic nitrite and potassic platinous chloride are warmed together. Its solutions are not precipitated either by alkalies or by sulphuretted hydrogen.—*Ammonic platinonitrite*, $(NH_4)_2Pt(NO_2)_4.2\mathbf{O}H_2$, crystallizes in prisms. It decomposes with sudden incandescence when heated.

COMPOUNDS OF PLATINUM WITH SULPHUR.

Platinous sulphide, $\mathbf{Pt}S''$.—This compound may be obtained as a black amorphous powder by passing sulphuretted hydrogen over moistened platinous chloride, or in a crystalline form by fusing platinous chloride with sodic carbonate and sulphur, and lixiviating the mass with water.

Platinic sulphide, $\mathbf{Pt}S''_2$.—Sulphuretted hydrogen precipitates, from solutions of platinic salts, black platinic sulphide, and this compound then unites with a further quantity of the gas to form light-brown hydric platinic sulphide, an unstable compound which parts with sulphuretted hydrogen when exposed to the air.—By fusing a mixture of spongy platinum, potassic carbonate, and sulphur, and extracting the mass with water, an insoluble *dipotassic diplatinous sulphodiplatinate*, $\left\{\begin{matrix}\mathbf{Pt}Pts''Ks\\ \mathbf{Pt}Pts''Ks\end{matrix}\right.$, is obtained in thin lead-gray six-sided tablets. When heated in a current of gaseous hydrochloric acid, this compound evolves sulphurretted hydrogen, and is converted into potassic chloride and a platinic sulphide of the formula $Pt_2S''_3$ (possibly, however, $Pt_4S''_6 = \left\{\begin{matrix}\mathbf{Pt}Pts'' \\ \mathbf{Pt}Pts''\end{matrix}S''\right)$, which remains as a steel-gray powder on extracting the mass with water.

AMMONIUM COMPOUNDS OF PLATINUM (PLATINAMINES).

Platinum forms a remarkable class of ammonium bases, the salts of which may be empirically formulated as double compounds of platinum salts with two or more molecules of ammonia. In this respect these compounds resemble the cobaltamines (*q.v.*). They have been divided into no fewer than twelve distinct classes. The members of one class are sometimes isomeric with those of another class. A complete account of these compounds would go beyond the scope of the present work. The following will serve as examples:

Platosotetrammonic chloride (*chloride of "Reiset's first base"*) is obtained in colorless prisms of the formula $\left\{\begin{array}{l} NH_2(N^vH_4)Cl \\ Pt'' \\ NH_2(N^vH_4)Cl \end{array}\right.,OH_2$, when platinous chloride is dissolved in an excess of boiling aqueous ammonia and the solution evaporated. It forms with platinous chloride an insoluble double salt, crystallizing in dark green needles of the formula $\left\{\begin{array}{l} NH_2(N^vH_4)Cl \\ Pt'' \\ NH_2(N^vH_4)Cl \end{array}\right.,PtCl_2$, also known as the *green salt of Magnus.* This compound, which is interesting as the first discovered of the platinum ammonium compounds, may be obtained direct by supersaturating with ammonia a hot solution of platinous chloride in hydrochloric acid.—*Platosotetrammonic hydrate,* $\left\{\begin{array}{l} NH_2(N^vH_4)Ho \\ Pt'' \\ NH_2(N^vH_4)Ho \end{array}\right.$, is prepared by precipitating a solution of the sulphate with baric hydrate and evaporating the filtrate. It crystallizes in deliquescent needles. It acts as a caustic, absorbs carbonic anhydride from the air, and precipitates the metals as hydrates from the solutions of their salts.

Platosodiammonic chloride (*chloride of "Reiset's second base"*), $\left\{\begin{array}{l} NH_3Cl \\ Pt'' \\ NH_3Cl \end{array}\right.$.—This compound, which is isomeric with the green salt of Magnus, is formed when platosotetrammonic chloride is heated to between 220° and 270° C. (430–518° F.). It forms microscopic, yellow rhombohedra. It is sparingly soluble in water, and is formed as a precipitate when hydrochloric acid is added to the solutions of other salts of this base. Both the hydrate and the oxide are known. The latter compound, which has the formula $\left\{\begin{array}{l} NH_3- \\ Pt''\quad O \\ NH_3- \end{array}\right.$, is obtained by heating platosotetrammonic hydrate to 110° C.

Platinodiammonic chloride (*chloride of "Gerhardt's base"*), $\left\{\begin{array}{l} NH_2Cl \\ PtCl_2 \\ NH_2Cl \end{array}\right.$, is formed by the direct union of platosodiammonic chloride with chlorine, when the gas is passed through water in which this salt is suspended. It crystallizes in minute yellow octahedra.

Platinotetrammonic chloride (*"Gros' chloride"*) $\left\{\begin{array}{l} NH_2(N^vH_4)Cl \\ PtCl_2 \\ NH_2(N^vH_4)Cl \end{array}\right.$.—This compound is formed in a similar manner by the union of platosotetrammonic chloride with chlorine, or by treating platinodiammonic chloride with ammonia. It crystallizes in yellow octahedra of the regular system.

General Properties and Reactions of the Compounds of Platinum.—a. *Platinous Compounds.*—These are of subordinate interest. The platinous salts are of a red, brown, or green color.

b. *Platinic Compounds.*—The platinic salts have a yellow color. With *caustic soda* they give a yellow precipitate of platinic hydrate, soluble

in an excess of the alkali. *Sulphuretted hydrogen* precipitates, slowly in the cold, more rapidly on heating, platinic sulphide, which is soluble in a large excess of ammonic sulphide. *Potassic chloride* and *ammonic chloride* produce yellow crystalline precipitates of potassic platinic chloride and ammonic platinic chloride. *Stannous chloride* in acid solutions produces a dark coloration, owing to the reduction of the platinic salt to the platinous stage, but no separation of metallic platinum occurs. *Ferrous sulphate* precipitates metallic platinum, but only after protracted boiling. *Oxalic acid* does not reduce the salts of platinum (separation from gold); but by boiling with soluble *formates* in alkaline solution, metallic platinum is precipitated. All platinum compounds, when ignited with access of air, are converted into metallic platinum.

PALLADIUM, Pd.

Atomic weight = 105.7. *Molecular weight unknown.* *Sp. gr.* 11.4. *Atomicity* $''$ *and*^{iv}. *Evidence of atomicity:*

Palladous chloride, ...	$Pd''Cl_2$.
Palladous oxide, ...	$Pd''O$.
Palladic chloride, ...	$Pd^{iv}Cl_4$.
Palladic oxide, ...	$Pd^{iv}O_2$.

History.—Palladium was discovered by Wollaston in 1803.

Occurrence.—Granules of this metal, sometimes in the form of octahedra, occur in the platinum ore of Brazil. Alloyed with platinum and other metals, it occurs in all ores of platinum.

Preparation.—One method of separation of palladium from the other metals of the platinum-group with which it occurs, depends upon the fact that palladium is precipitated as insoluble palladous iodide by the careful addition of potassic iodide to the solution of palladous chloride. The other metals remain in solution. An excess of the precipitant is to be avoided, as it dissolves the palladous iodide. The iodide loses its iodine when strongly heated, and is converted into spongy palladium.—In order to extract the palladium from platinum ore, the solution which is obtained after dissolving the ore in aqua-regia and removing the platinum by precipitation with ammonic chloride, is treated with mercuric cyanide. In this way a precipitate of palladous cyanide is produced, which by ignition may be converted into the metal.

Properties.—Palladium is a silver-white lustrous metal. It sometimes occurs crystallized, either in octahedra or in small hexagonal plates. Palladium is the most fusible of the platinum metals and can be welded at a red heat more readily than platinum. When heated to low redness it undergoes superficial oxidation, and assumes a blue color, but at a higher temperature regains its lustre. It is soluble in hot nitric acid and in hot concentrated sulphuric acid. Hydrochloric acid dissolves spongy palladium in presence of air. It is not altered by exposure to air or to sulphuretted hydrogen.—Spongy palladium, like spongy platinum, is capable of effecting the combination of oxygen and hydrogen when introduced into a mixture of these gases. If the two gases are present in the proportions necessary to form water, the palladium

becomes red-hot, causing explosion; but if a considerable excess of oxygen is present or if air be substituted for oxygen, the combination takes place slowly at ordinary temperatures without explosion. In the case of a mixture of hydrogen, marsh-gas and air, it is possible to effect the slow combustion of the hydrogen, leaving the marsh-gas untouched, and in this way the hydrogen present in a mixture of combustible gases may be determined.—If a piece of palladium foil be heated in the flame of a spirit lamp, or in a coal-gas flame, the foil becomes covered with cauliflower-like excrescences of soot, and when these are burnt they leave a skeleton of filaments of metallic palladium, whilst the foil is found to have become porous. In like manner, when spongy palladium is heated in a current of ethylene, the gas is decomposed with separation of carbon at a temperature at which ethylene alone is perfectly stable. These phenomena probably depend upon the affinity of palladium for hydrogen, palladium hydride (*q.v.*) being successively formed and decomposed. In the formation of this compound carbon is liberated from the gases present in the flame; in its decomposition the palladium disintegrates.

Uses.—Palladium is used for the graduated scales of physical instruments and also for coating silver goods.

COMPOUND OF PALLADIUM WITH HYDROGEN.

Palladium hydride, Pd_4H_2.—This compound is formed by the direct union of its elements when palladium is heated in a current of hydrogen, or when this metal is employed as negative electrode in the electrolysis of dilute sulphuric acid.—Palladium hydride is a lustrous metallic mass with a specific gravity of 11.06. It conducts electricity. It parts with its hydrogen only very gradually at ordinary temperatures, but rapidly on heating. On exposure to the air in a finely divided state it becomes red hot, owing to the absorption of oxygen and oxidation of the hydrogen to water. It acts as a reducing agent; thus it precipitates metallic mercury from solutions of the salts of that metal.

COMPOUNDS OF PALLADIUM WITH THE HALOGENS.

a. Palladous Compounds.

Palladous chloride, $\mathbf{Pd}Cl_2$.—When a solution of palladium in aqua-regia is evaporated to dryness, the palladic chloride which is at first formed is decomposed and converted into palladous chloride, which remains as a brown deliquescent mass. This compound may also be obtained as a red crystalline sublimate by heating palladous sulphide ($\mathbf{Pd}S''$) in a current of dry chlorine. In this form it dissolves only slowly in water.—Like the corresponding platinum compound it forms numerous double chlorides. *Potassic palladous chloride* has the formula $\mathbf{Pd}Cl_2,2KCl$.

Palladous bromide is not known in the pure state.

Palladous iodide, $\mathbf{Pd}I_2$.—This compound is precipitated as a black powder when potassic iodide is added to solutions of palladous chloride

or nitrate. It is soluble in an excess of potassic iodide. Iodine may be estimated as palladous iodide in presence of chlorine and bromine.

b. Palladic Compounds.

Of these only the chloride is known, and this has been obtained only in solution. It forms, however, well-characterized double salts, corresponding to those of platinum: thus *potassic palladic chloride*, $PdCl_4$,$2KCl$, which crystallizes in brownish-red octahedra; and *ammonic palladic chloride*, $PdCl_4,2NH_4Cl$, which forms a sparingly soluble red crystalline powder.

COMPOUNDS OF PALLADIUM WITH OXYGEN.

Hypopalladous oxide, .	$\left\{\begin{matrix} Pd \\ Pd \end{matrix}\right. O$.	$\begin{matrix} Pd \\ \vert \\ Pd \end{matrix} > O$.
Palladous oxide, . . .	PdO.	$Pd{=}O$.
Palladic oxide, . . .	PdO_2.	$O{=}Pd{=}O$.

Hypopalladous oxide, $'Pd'_2O$, is obtained as a black powder by heating palladous hydrate to low redness as long as oxygen is evolved. Acids decompose it with separation of metallic palladium and formation of palladous salts. When heated in a current of hydrogen it is reduced with sudden incandescence.

Palladous oxide, PdO, is prepared by careful ignition of the nitrate. It forms a black powder which dissolves with difficulty in acids. When brought into hydrogen at ordinary temperatures it is instantaneously reduced with incandescence.—Alkaline carbonates precipitate from solutions of palladous salts a dark-brown hydrate, which dissolves readily in acids.

Palladic oxide, PdO_2, is a black powder obtained by boiling potassic palladic chloride with caustic potash and washing the precipitate with hot water.

PALLADOUS OXY-SALTS.

Palladous nitrate, N_2O_4Pdo'', is prepared by dissolving the metal or the oxide in nitric acid. On evaporation the solution deposits long brown deliquescent prisms.

Palladous sulphate, $SO_2Pdo'',2OH_2$, is obtained by dissolving the metal in sulphuric acid, with the addition of nitric acid, and evaporating. It forms brown soluble crystals, which are decomposed by excess of water with separation of a basic salt.

A series of ammonium compounds of palladium, corresponding with those of platinum, is known.

COMPOUNDS OF PALLADIUM WITH SULPHUR.

These correspond with the oxides.

Hypopalladous sulphide, $'Pd'_2S''$, is formed when either palladous sulphide or palladic sulphide is heated in a current of carbonic anhydride. It is most readily obtained by fusing together at a red heat a mixture of palladous sulphide, potassic carbonate, sulphur, and ammonic chloride. On dissolving the mass in water, hypopalladous sulphide remains as a brittle, green, metallic regulus. It is only slowly attacked by nitric acid.

Palladous sulphide, PdS'', is obtained as a grayish-white metallic mass by heating the metal in the vapor of sulphur, when combination occurs with incandescence. The same compound is precipitated as a black amorphous powder when sulphuretted hydrogen is passed into solutions of palladous salts.

Palladic sulphide, PdS''_2.—When palladous sulphide is fused with sulphur and sodic carbonate, *sodic sulphopalladate,* $PdS''\,Nas_2$, is formed. On decomposing this compound with hydrochloric acid, palladic sulphide is obtained as a dark-brown powder. It dissolves readily in aqua-regia.

General Properties and Reactions of the Compounds of Palladium.—The palladous salts are for the most part soluble, yielding solutions which, when concentrated, are brown or reddish-brown, when dilute, yellow. Both *sulphuretted hydrogen* in acid solution and *ammonic sulphide* precipitate black palladous sulphide, insoluble in excess of ammonic sulphide, but soluble in boiling hydrochloric acid. *Caustic alkalies* precipitate brown basic salts of palladium, soluble in an excess of the alkali on heating. *Ammonia* gives a flesh-colored precipitate of a palladammonium compound, soluble in excess of ammonia. *Potassic iodide* precipitates black palladous iodide. *Ferrous sulphate* precipitates metallic palladium, the action being facilitated by heat. All palladium compounds yield on ignition in air metallic palladium.

IRIDIUM, Ir.

Atomic weight = 192.5. *Molecular weight unknown. Sp. gr.* 22.38. *Atomicity* $''$ *and* ^{iv}, *also a pseudo-triad. Evidence of atomicity:*

Iridous sulphide, ...	$Ir''S''$.
Di-iridic hexachloride, ...	$'Ir'''_2Cl_6$.
Di-iridic trioxide, ...	$'Ir'''_2O_3$.
Iridic chloride, ...	$Ir^{iv}Cl_4$.
Iridic oxide, ...	$Ir^{iv}O_2$.

History.—Iridium was discovered in 1804 by Smithson Tennant.

Occurrence.—Iridium occurs in most ores of platinum in the form of granules of the alloys platiniridium and osmiridium.

Extraction.—For the preparation of iridium the residue which remains when the platinum ore is treated with aqua-regia is employed. This residue, which consists chiefly of iridium and osmium, but contains small quantities of all the other platinum metals, is fused with from 20 to 30 times its weight of zinc. On dissolving the zinc in hydrochloric acid, the platinum metals remain as a fine powder. This powder is mixed with from 3 to 4 parts of anhydrous baric chloride, and the mixture is heated to low redness in a current of dry chlorine. On dissolving in water, ruthenium remains behind, whilst the other platinum metals dissolve as double chlorides of barium with the platinum metal. Sulphuric acid is then added so as exactly to precipitate the barium. The liquid, which now contains the platinum metals as chlorides, is heated in an atmosphere of hydrogen in a flask on a water-bath. In this way the metals are reduced from their aqueous solution. During the whole of this operation air must be carefully excluded, as the finely divided metals would bring about the explosive combination of the hydrogen with the oxygen of the air. Platinum and palladium

are first reduced, then rhodium. Before the iridium is precipitated it undergoes reduction to di-iridic hexachloride, $'Ir'''_2Cl_6$, the presence to which is manifested by an olive-green coloration of the liquid. At this point the operation is interrupted, and after filtering off the reduced metals, the iridium is precipitated from the filtrate by first oxidizing it with nitric acid to iridic chloride, $IrCl_4$, and then adding a solution of potassic chloride, with which it forms a black, almost insoluble crystalline precipitate of potassic iridic chloride, $IrCl_4,2KCl$. This on ignition yields spongy iridium. A trace of ruthenium may be removed by fusing the spongy metal with nitre. On lixiviating the fused mass with water the ruthenium dissolves as potassic ruthenate, leaving the iridium.

Properties.—Iridium is a white metal, which when polished has a lustre resembling that of steel. It is harder than platinum, and much more brittle. It is also more refractory than platinum, but may be fused in the oxyhydrogen flame. Very finely divided iridium (iridium black) dissolves in aqua-regia and oxidizes when heated in air. Compact iridium is not attacked under any of these conditions, but may be oxidized by fusion with potassic hydrate to which nitre or potassic chlorate has been added. *Iridium black* is obtained as an impalpable powder by exposing an alcoholic solution of di-iridic sulphate to sunlight. It is more energetic in its catalytic action than platinum black. A small quantity brought upon paper moistened with alcohol causes ignition.

Uses.—An alloy of 1 part of iridium with 9 parts of platinum is extremely hard and elastic, capable of taking a high polish, and unalterable in air. It has been employed in the preparation of standard measures of length. Gold pens are sometimes tipped with an alloy of iridium and osmium.

COMPOUNDS OF IRIDIUM WITH THE HALOGENS.

a. Di-iridic Compounds.

Di-iridic hexachloride, $'Ir'''_2Cl_6$.—This compound is formed when the metal is heated in chlorine. It is most readily obtained by heating one of its alkaline double chlorides, such as potassic di-iridic chloride, $'Ir'''_2Cl_6,6KCl$, with concentrated sulphuric acid and pouring the cooled liquid into water, when the chloride separates as a pale olive-green precipitate, insoluble in water and in acids. It may be obtained in a soluble form by treating a solution of iridic chloride with sulphurous anhydride until the solution has become green.—The alkaline double chlorides are formed when the corresponding iridic double chlorides are reduced in aqueous solution with sulphurous anhydride or sulphuretted hydrogen. *Potassic di-iridic chloride,* $'Ir'''_2Cl_6,6KCl,6OH_2$, *sodic di-iridic chloride,* $'Ir'''_2Cl_6,6NaCl,24OH_2$, and *ammonic di-iridic chloride,* $'Ir'''_2Cl_6,6NH_4Cl, 3OH_2$, all form olive-green crystals, soluble in water, insoluble in alcohol.

Di-iridic hexabromide, $'Ir'''_2Br_6,8OH_2$, is deposited in light olive-green six-sided crystals when a solution of iridic hydrate, $IrHo_4$, in hydrobromic acid is evaporated. The iridic bromide does not appear to be capable of existing: the solution evolves bromine and contains the lower bromide. Di-iridic hexabromide forms double bromides corresponding with the double chlorides.

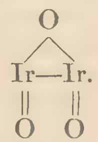
b. Iridic Compounds.

Iridic chloride, $IrCl_4$, is obtained as a black mass by dissolving iridium black, di-iridous trioxide, or di-iridic hexachloride in aqua-regia, and evaporating the solution at a temperature below 40° C. (104° F.). On heating to a higher temperature chlorine is evolved, and the solution contains the lower chloride.—It forms with the chlorides of the alkalies double chlorides, isomorphous with those of platinum. *Potassic iridic chloride*, $IrCl_4,2KCl$, and *ammonic iridic chloride*, $IrCl_4,2NH_4Cl$, crystallize in minute dark-red octahedra, sparingly soluble in cold water. *Sodic iridic chloride*, $IrCl_4,2NaCl$, is readily soluble in water, and forms black tabular crystals or prisms.

Iridic bromide, $IrBr_4$, is not known; but numerous double bromides corresponding with the double chlorides have been prepared.

Iridic iodide, IrI_4, is obtained as a black powder by the action of potassic iodide upon the solution of the chloride in hydrochloric acid.

COMPOUNDS OF IRIDIUM WITH OXYGEN.

Di-iridic trioxide, $'\mathrm{Ir}'''_2O_3$. 

Iridic oxide, . . IrO_2. $O{=}Ir{=}O$.

Di-iridic trioxide, $'\mathrm{Ir}'''_2O_3$.—This compound is formed when finely divided iridium is heated in air. At a higher temperature it is again decomposed into oxygen and metal. It is most readily prepared by heating a mixture of potassic iridic chloride and sodic carbonate to low redness:

$$\underset{\text{Potassic iridic chloride.}}{2IrCl_4,(KCl)_2} + \underset{\text{Sodic carbonate.}}{4COnao_2} = \underset{\text{Di-iridic trioxide.}}{'\mathrm{Ir}'''_2O_3} + \underset{\text{Sodic chloride.}}{8NaCl} +$$

$$\underset{\text{Potassic chloride.}}{4KCl} + \underset{\text{Carbonic anhydride.}}{4CO_2} + O.$$

On extracting the mass with water the oxide remains behind as a black powder. Hydrogen, even at ordinary temperatures, reduces it to the metallic state.—When a solution of potassic di-iridic chloride is precipitated by a small quantity of caustic potash with exclusion of air, yellowish-green *di-iridic hexahydrate*, $'\mathrm{Ir}'''_2Ho_6$, is obtained. It is soluble in excess of alkali, and oxidizes on exposure to air.

Iridic oxide, IrO_2.—When moist di-iridic hexahydrate undergoes spontaneous oxidation by exposure to air, it is converted into *iridic hydrate*, $IrHo_4$. The same compound is obtained by precipitating iridic chloride with caustic alkali. It forms an indigo-blue powder, which is not atacked by dilute acids with the exception of hydrochloric. When carefully heated in a current of carbonic anhydride it is converted into iridic oxide, which is thus obtained as a black powder insoluble in acids.

OXY-SALTS OF IRIDIUM.

These are comparatively unimportant. Salts of the unknown *iridous oxide*, **Ir**O, have been prepared; thus a *sodic iridous sulphite* of the formula $\mathbf{S}_4O_4Nao_6Iro'',10\mathbf{O}H_2$ is known. An oxy-salt corresponding to di-iridic trioxide is *di-iridic trisulphite*, $\mathbf{S}_3O_3('Ir'''_2O_6)^{vi},6\mathbf{O}H_2$, which is obtained as a crystalline powder by dissolving the hexyhydrate in sulphurous acid and evaporating. No iridic oxy-salts are known.

Ammonium compounds of iridium corresponding with those of platinum have been prepared.

COMPOUNDS OF IRIDIUM WITH SULPHUR.

Iridous sulphide, $\mathbf{Ir}S''$, is obtained as a lustrous metallic mass when the metal is heated in the vapor of sulphur.

Di-iridic trisulphide, $'\mathbf{Ir}'''_2S''_3$, is obtained as a brown precipitate when sulphuretted hydrogen is passed into the solution of a di-iridic salt.

Iridic sulphide, $\mathbf{Ir}S''_2$.—This compound is prepared by heating the finely divided metal with sodic carbonate and sulphur, extracting the mass with water. The iridic sulphide remains as a black powder.

General Properties and Reactions of the Compounds of Iridium.—A not too dilute solution of an iridic salt yields with *ammonic chloride* a dark-red crystalline precipitate of ammonic iridic chloride. From the solution of an iridic salt *sulphuretted hydrogen* precipitates brown di-iridic trisulphide ($'\mathbf{Ir}'''_2S''_3$) with separation of sulphur. *Ferrous sulphate* decolorizes the solution of an iridic salt; *zinc* precipitates black spongy iridium.

RHODIUM, Rh.

Atomic weight = 104. *Molecular weight unknown. Sp. gr.* 12.1. *Atomicity* '' *and* ^{iv}, *also a pseudo-triad. Evidence of atomicity:*

Rhodous oxide, ...	$\mathbf{Rh}''O$.
Dirhodous hexachloride, ...	$'\mathbf{Rh}'''_2Cl_6$.
Dirhodous trioxide, ...	$'\mathbf{Rh}'''_2O_3$.
Rhodic hydrate, ...	$\mathbf{Rh}^{iv}Ho_4$.
Rhodic oxide, ...	$\mathbf{Rh}^{iv}O_2$.

History.—Rhodium was discovered by Wollaston in 1804, and afterwards investigated more thoroughly by Berzelius and Claus.

Occurrence.—The metal occurs in small quantity in platinum ore.

Extraction.—The only source of rhodium is the platinum residue already referred to. The mixture of platinum, palladium, and rhodium precipitated by hydrogen in the process of separating the platinum metals is redissolved in aqua-regia, and the platinum is precipitated by potassic chloride. After expelling the excess of acid, the rhodium may be precipitated as *sodic dirhodous sulphite*, $\mathbf{S}_6O_6Nao_6('Rh'''_2O_6)^{vi}$, by boiling the dilute solution with hydric sodic sulphite. The metal may be precipitated by reducing agents from the solutions of its salts and fused into a coherent mass in the oxyhydrogen furnace.

Properties.—Rhodium is a malleable metal, resembling aluminium in color and lustre. Its fusing-point lies between that of platinum and that of iridium. When heated in air it undergoes superficial oxidation. Pure rhodium is insoluble in all acids and in aqua-regia. If, however, it is alloyed with an excess of platinum, or with zinc, lead, and other oxidizable metals, aqua-regia dissolves it.

COMPOUND OF RHODIUM WITH CHLORINE.

Dirhodic hexachloride, $'\mathbf{Rh}'''_2Cl_6$.—This is the only halogen compound of rhodium which is known with certainty. The anhydrous chloride is formed when the finely divided metal is heated in chlorine. It is an insoluble rose-red powder. By dissolving dirhodic hexahydrate in hydrochloric acid and evaporating the solution, a dark-red hydrated chloride is obtained, which on heating is converted into the anhydrous chloride. Dirhodic hexachloride forms double salts with the alkaline chlorides.

COMPOUNDS OF RHODIUM WITH OXYGEN.

Rhodous oxide, .	$\mathbf{Rh}O$.	$Rh{=}O$.
Dirhodic trioxide,	$'\mathbf{Rh}'''_2O_3$.	$\begin{array}{ccc} & O & \\ & \diagup\ \diagdown & \\ Rh & — & Rh. \\ \Vert & & \Vert \\ O & & O \end{array}$
Rhodic oxide, .	$\mathbf{Rh}O_2$.	$O{=}Rh{=}O$.

Rhodous oxide, $\mathbf{Rh}O$.—This compound is formed with incandescence when the hexahydrate is heated. It is a dark-gray powder, insoluble in acids.

Dirhodic trioxide, $'\mathbf{Rh}'''_2O_3$, is obtained as a gray spongy lustrous mass by heating the nitrate. It does not dissolve in acids.—*Dirhodic hexahydrate* is prepared by the action of hot caustic potash upon sodic dirhodic chloride, $'\mathbf{Rh}'''_2Cl_6,6NaCl,3\mathbf{O}H_2$. It is a brownish-black gelatinous precipitate, difficultly soluble in acids. By the action of caustic soda upon the double chloride in the cold, yellow crystals of the hydrate $'\mathbf{Rh}'''_2Ho_6,2\mathbf{O}H_2$ are obtained. These dissolve readily in acids.

Rhodic oxide, $\mathbf{Rh}O_2$, is obtained by repeatedly fusing finely divided rhodium with caustic potash and nitre. It is a brown powder, insoluble in acids.

OXY-SALTS OF RHODIUM.

These are derived from dirhodic trioxide.

Dirhodic nitrate, $\mathbf{N}_6O_{12}('Rh'''_2O_6)^{vi}$, is uncrystallizable.

Dirhodic sulphate, $\mathbf{S}_3O_6('Rh'''_2O_6)^{vi},12\mathbf{O}H_2$, is obtained as a yellow soluble crystalline mass by evaporating the solution of the yellow hydrate in sulphuric acid.

Dirhodic sulphite, $\mathbf{S}_3O_3('Rh'''_2O_6)^{vi},6\mathbf{O}H_2$, remains as a yellow, difficultly crystallizable mass when the solution of the yellow hydrate in sulphurous acid is evaporated.

Ammonium compounds of rhodium have been prepared.

COMPOUND OF RHODIUM WITH SULPHUR.

Rhodous sulphide, $\mathbf{Rh}S''$.—This compound is formed as a fused metallic mass when rhodium is heated in the vapor of sulphur.

General Properties and Reactions of the Compounds of Rhodium.—The solutions of the dirhodic salts are sometimes rose-colored, sometimes yellow. *Caustic alkalies* give a yellow precipitate, which, on heating the liquid with the precipitate, becomes brownish-

black, and then consists of dirhodic hexahydrate. *Sulphuretted hydrogen* and *ammonic sulphide* give, after protracted action aided by heat, a brown precipitate, probably a dirhodic trisulphide ($'Rh'''_2S''_3$). *Potassic iodide* precipitates sparingly soluble yellow dirhodic hexiodide. *Zinc* precipitates black metallic rhodium.

OCTAD ELEMENTS.

OSMIUM, Os.

Atomic weight =198.6? *Molecular weight unknown. Sp. gr.* 22.477. *Atomicity*'', ^{iv},, ^{vi}, *and* ^{viii}, *also a pseudo-triad. Evidence of atomicity:*

Osmous oxide,	$Os''O$.
Diosmic trioxide,	$'Os'''_2O_3$.
Osmic chloride,	$Os^{iv}Cl_4$.
Potassic osmate,	$Os^{vi}O_2Ko_2$.
Osmic peroxide,	$Os^{viii}O_4$.

History.—Osmium was discovered in 1804, by Smithson Tennant.

Occurrence—It occurs alloyed with iridium, in the ores of platinum. This alloy, known as *osmiridium*, remains behind when the ore is treated with aqua-regia.

Extraction.—If in the preparation of iridium (p. 595) the mixture of the finely divided platinum metals with baric chloride be heated in a current of *moist* chlorine, the greater part of the osmium is volatilized as osmic peroxide, and may be condensed in a cooled receiver. The rest of the osmium may be recovered if the solution containing the chlorides of the platinum metals, which remains after the precipitation of the barium in the above operation (p. 595), be mixed with excess of nitric acid and distilled. The aqueous distillate contains the osmium as peroxide. On adding to the solution of the peroxide ammonia and ammonic sulphide, the osmium is precipitated as osmic persulphide, OsS''_4. This is mixed with sodic chloride and heated in a slow current of chlorine. On extracting with water, a solution of sodic osmic chloride, $OsCl_4,2NaCl$, is obtained, from which on the addition of ammonic chloride the osmium is precipitated as ammonic osmic chloride, $OsCl_4,2NH_4Cl$. When this is ignited in a covered crucible, metallic osmium is obtained as a spongy mass.

By fusing spongy osmium with tin, and dissolving the tin with hydrochloric acid, osmium is obtained in crystals.

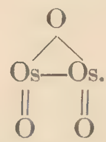
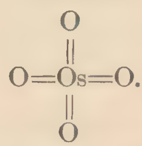
Properties.—Osmium is not fusible at the highest temperatures, though it is volatile when heated to the fusing-point of iridium. Heated in air it burns, forming osmic peroxide, and if a quantity of finely divided osmium be ignited at one point, the ignition is propagated throughout the mass. Aqua-regia also oxidizes the finely divided metal to peroxide. Crystallized osmium forms cubes. In this condition it has a sp. gr. of 22.477, and is therefore the heaviest substance known.

COMPOUNDS OF OSMIUM WITH CHLORINE.

Diosmic hexachloride, $'Os'''_2Cl_6$, is known only in the form of its double chloride. *Potassic diosmic chloride*, $'Os'''_2Cl_6,6KCl,6OH_2$, forms dark-red crystals.

Osmic chloride, $OsCl_4$, is obtained as a red sublimate when the metal is heated in dry chlorine. It dissolves in water yielding a yellow solution, which gradually deposits lower oxides of osmium, and becomes colorless. The solution then contains osmic peroxide and hydrochloric acid. Osmic chloride forms double salts.

COMPOUNDS OF OSMIUM WITH OXYGEN.

Osmous oxide, .	OsO.	$Os{=}O$.
Diosmic trioxide,	$'Os'''_2O_3$.	
Osmic oxide, .	OsO_2.	$O{=}Os{=}O$.
Osmic peroxide, .	OsO_4.	

Osmous oxide, OsO, is obtained as a grayish-black powder, insoluble in acids, by heating a mixture of osmous sulphite, $SOOso''$, with sodic carbonate, in a current of carbonic anhydride.

Diosmic trioxide, $'Os'''_2O_3$, is prepared by heating potassic diosmic chloride with sodic carbonate. It is a black powder, insoluble in acids.

Osmic oxide, OsO_2, is obtained in a similar way from potassic osmic chloride, $OsCl_4,2KCl$. Thus prepared it forms a grayish-black powder; but by heating osmic hydrate in a current of carbonic anhydride, it is obtained in copper-colored masses, possessing a metallic lustre.—*Osmic hydrate*, $OsHo_4$, is formed as a black precipitate when reducing agents, such as alcohol, are added to the aqueous solution of osmic peroxide.

Osmic peroxide (*Osmic anhydride, Osmic acid*), OsO_4. *Molecular volume* $\square\square$.—This remarkable compound is formed when the finely divided metal, or any of the lower oxides of osmium, is heated in air or oxygen, or dissolved either in nitric acid or in aqua-regia. If the finely divided metal has been previously ignited with exclusion of air, these solvents are without action upon it. Osmic peroxide forms long colorless prisms or needles, with a powerful and irritating odor. They sublime even at ordinary temperatures, and when gently heated fuse to a colorless liquid, which boils without decomposition at 100° C. Osmic peroxide dissolves in water, yielding a neutral solution with a powerful odor and a burning taste. Alcohol and ether precipitate from the solution osmic hydrate. Sulphurous anhydride colors the solution in turn

yellow, brown, green, and finally blue, at which point the liquid contains osmous sulphite. The vapor of osmic peroxide, even when largely diluted with air, attacks the lungs, producing dangerous inflammation of the mucous membrane. It also acts violently upon the eyes, and may even cause blindness, owing to the deposition of a film of metallic osmium upon the eye. Brought in contact with the skin, osmic peroxide produces a painful eruption, which is very difficult to heal.

OXY-SALTS OF OSMIUM.

These are few in number, and unimportant.

Osmous sulphite, $\mathbf{S}OOso''$, is obtained by passing sulphurous anhydride into a solution of osmic peroxide until the solution assumes a blue color, and then adding sodic sulphate. The osmium salt, which is sparingly soluble in a solution of sodium sulphate, is deposited as a dark-blue precipitate.—*Hydric potassic osmous sulphite*, $\mathbf{S}_5O_5Ho_2Ko_6Oso'',4\mathbf{O}H_2$, is obtained as a rose-red precipitate by heating a solution of potassic diosmic chloride (p. 601) with potassic sulphite.

THE OSMATES.

Neither osmic acid, $\mathbf{Os}O_2Ho_2$, nor its anhydride, $\mathbf{Os}O_3$, is known; but some of the salts of osmic acid have been prepared.

Potassic osmate, $\mathbf{Os}O_2Ko_2,2\mathbf{O}H_2$, is obtained by adding alcohol or potassic nitrite to a sufficiently concentrated solution of the peroxide in potassic hydrate. The peroxide is reduced and unites with the alkali to form potassic osmate, which gradually separates as a dark-red crystalline powder.

Baric osmate, $\mathbf{Os}O_2Bao''$, forms black lustrous prismatic crystals.

COMPOUNDS OF OSMIUM WITH SULPHUR.

The sulphides of osmium have been but little studied. Osmium combines with sulphur when heated in its vapor, and sulphuretted hydrogen precipitates osmium as sulphide from its solutions. From solutions containing osmium in its lower stages of oxidation a yellow sulphide is precipitated; whilst solutions of the peroxide give a brown precipitate of *osmic persulphide*, $\mathbf{Os}S''_4$.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF OSMIUM.—Osmium and its compounds are best characterized by the readiness with which they yield the volatile peroxide, recognizable by its powerful odor. All osmium compounds when boiled with nitric acid give off vapors of the peroxide.

RUTHENIUM, Ru.

Atomic weight = 104. *Molecular weight unknown. Sp. gr.* 12.26. *Atomicity* $''$, ^{iv}, ^{vi}, *and* ^{viii}, *also a pseudo-triad and a pseudo-heptad. Evidence of atomicity:*

Ruthenous oxide, ...	$\mathbf{Ru}''O$.
Diruthenic hexachloride, ...	$'\mathbf{Ru}'''_2Cl_6$.
Ruthenic chloride, ...	$\mathbf{Ru}^{iv}Cl_4$.
Potassic ruthenate, ...	$\mathbf{Ru}^{vi}O_2Ko_2$.
Potassic perruthenate, ...	$'\mathbf{Ru}^{vii}_2O_6Ko_2$.
Ruthenic peroxide, ...	$\mathbf{Ru}^{viii}O_4$.

History.—Ruthenium was first directly recognized as a new metal by Claus, in 1845.

Occurrence.—Ruthenium is found alloyed with the other platinum metals in platinum ore. Combined with sulphur it occurs as the mineral *laurite*, $'\mathbf{Ru}'''_2S''_3$.

Extraction.—The insoluble residue of ruthenium obtained in the preparation of iridium (p. 596) may be purified by fusion with a mixture of potassic hydrate and nitre. On treating the fused mass with water the ruthenium goes into solution as potassic ruthenate. The orange-red solution is boiled with an excess of nitric acid until the color has disappeared; in this way the ruthenium is precipitated as diruthenic trioxide, which by ignition in a graphite crucible is converted into the metal. It may be fused into a coherent mass in a lime crucible by means of the oxyhydrogen flame.

Properties.—Ruthenium is a white metal, hard and brittle like iridium, and still more difficultly fusible than this metal. The finely divided metal is oxidized when heated in air. Aqua-regia attacks it only very slowly.

COMPOUNDS OF RUTHENIUM WITH THE HALOGENS.

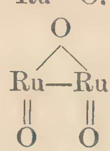
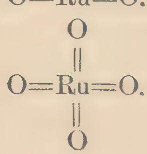
Ruthenous chloride, $\mathbf{Ru}Cl_2$, is prepared by gently heating the finely divided metal in a current of chlorine. It is a black crystalline powder, insoluble in acids.

Diruthenic hexachloride, $\mathbf{Ru}'''_2Cl_6$, is obtained as a yellow crystalline deliquescent mass by dissolving diruthenic hexahydrate in hydrochloric acid and evaporating to dryness. It forms double chlorides with the chlorides of the alkalies: $'\mathbf{Ru}'''_2Cl_6,4KCl$, and $'\mathbf{Ru}'''_2Cl_6,4NH_4Cl$.

Diruthenic hexiodide, $'\mathbf{Ru}'''_2I_6$, is obtained as a black powder when potassic iodide is added to a solution of the chloride.

Ruthenic chloride, $\mathbf{Ru}Cl_4$, is obtained as a reddish-brown mass by dissolving ruthenic hydrate in hydrochloric acid and evaporating. It forms with the chlorides of the alkalies double chlorides, corresponding with those of platinic chloride. The potassium compound has the formula $\mathbf{Ru}Cl_4,2KCl$, and crystallizes in red regular octahedra.

COMPOUNDS OF RUTHENIUM WITH OXYGEN.

Ruthenous oxide, .	$\mathbf{Ru}O$.	$Ru{=}O$.
Diruthenic trioxide,	$'\mathbf{Ru}'''_2O_3$.	
Ruthenic oxide, .	$\mathbf{Ru}O_2$.	$O{=}Ru{=}O$.
Ruthenic peroxide,	$\mathbf{Ru}O_4$.	

Ruthenous oxide, **Ru**O, is obtained by calcining ruthenous chloride with sodic carbonate and extracting the cooled mass with water, when the oxide remains as a dark-gray powder insoluble in acids.

Diruthenic trioxide, $'\mathbf{Ru}'''_2O_3$, is formed when finely divided ruthenium is heated for a considerable time in contact with air. It is a bluish-black powder, which does not part with its oxygen even at a white heat. Acids are without action upon it.—*Diruthenic hexahydrate*, $'\mathbf{Ru}'''_2Ho_6$, is obtained as a dark-brown precipitate when a caustic alkali is added to a solution of diruthenic hexachloride. It dissolves in acids, yielding a yellow solution.

Ruthenic oxide, $\mathbf{Ru}O_2$, is prepared by heating ruthenic sulphide in air or by heating finely divided ruthenium very strongly in a current of air. In the latter case the oxide sublimes in green quadratic pyramids, isomorphous with those of tin-stone and rutile.—*Ruthenic hydrate*, $\mathbf{Ru}Ho_4,3\mathbf{O}H_2$, is a dark-red powder obtained by precipitating solutions of ruthenic salts with caustic alkali. It deflagrates on heating.

Ruthenic peroxide, $\mathbf{Ru}O_4$.—In order to prepare this compound a solution of potassic ruthenate (*infra*) is introduced into a retort and a rapid current of chlorine is passed through the liquid. In the oxidation which occurs considerable heat is evolved, and the ruthenic peroxide which is formed volatilizes in the current of chlorine, and condenses in the neck of the retort and in the well-cooled receiver as a yellow crystalline mass consisting of rhombic prisms. It is purified by fusion under a small quantity of water. The crystals fuse at 40° C. (104° F.) to a liquid which boils a little above 100° C. yielding a golden-yellow vapor with an extremely irritating odor. The experiment of distilling the peroxide alone ought never to be performed, as the heated substance is apt to decompose with violent explosion. The compound ought to be volatilized as above at a lower temperature in a current of some gas. Moist ruthenic peroxide is rapidly decomposed with evolution of oxygen and formation of diruthenic hexahydrate; the dry substance is more stable. It is sparingly soluble in water.

OXY-SALTS OF RUTHENIUM.

These are unimportant and have been little studied.

Ruthenic sulphate, $\mathbf{S}_2O_4\mathrm{Ruo}^{iv}$, is obtained by oxidizing ruthenic sulphide with nitric acid and evaporating the solution. It is a deliquescent powder resembling in appearance mosaic gold.

RUTHENATES AND PERRUTHENATES.

Two oxides of ruthenium—ruthenic anhydride, $\mathbf{Ru}O_3$, and perruthenic anhydride, $\mathbf{Ru}_2O_7$—intermediate between ruthenic oxide and ruthenic peroxide, are known only in the form of the salts of their acids.

Potassic ruthenate, $\mathbf{Ru}O_2Ko_2$, is formed when finely divided ruthenium is fused with a mixture of caustic potash and nitre or potassic chlorate. It dissolves in water, yielding a reddish-yellow solution with an astringent taste. The solution colors organic substances black.

Potassic perruthenate, $'\mathbf{Ru}^{vii}_2O_6Ko_2$, is formed when chlorine acts upon the preceding salt in aqueous solution :

$$2RuO_2Ko_2 + Cl_2 = {}'Ru^{vii}{}_2O_6Ko_2 + 2KCl.$$

Potassic ruthenate.		Potassic perruthenate.	Potassic chloride.

The dark-green solution deposits small black crystals isomorphous with potassic permanganate.

Ammonium compounds of ruthenium have been prepared.

COMPOUND OF RUTHENIUM WITH SULPHUR.

Diruthenic trisulphide, $'Ru'''S''_3$.—This compound occurs as the mineral *laurite* in some platinum ores. It crystalizes in octahedra. A part of the ruthenium is generally replaced by osmium. The same compound is obtained as a dark metallic powder by precipitating solutions of ruthenium salts with sulphuretted hydrogen and drying the precipitate in a current of carbonic anhydride.

General Properties and Reactions of the Compounds of Ruthenium.—Solutions of ruthenic salts yield with *potassic chloride* and *ammonic chloride* dark-red crystalline precipitates of the corresponding double chlorides. *Sulphuretted hydrogen* first changes the color of the liquid to blue, and afterwards precipitates brown diruthenic trisulphide. *Zinc* also changes the color of the solution to blue, and afterwards decolorizes it with precipitation of black metallic ruthenium. The formation of a volatile peroxide (p. 604) is common to this metal and osmium.

CHAPTER XXXIX.

TETRAD ELEMENTS.

Section V.

LEAD, Pb.

Atomic weight = 206.5. *Molecular weight unknown. Sp. gr.* 11.37. *Fuses at* 326° C. (619° F.). *Boils at a white heat. Atomicity* '' *and* ^{iv}. *Sometimes also a pseudo-triad. Evidence of atomicity:*

Plumbic chloride,	$Pb''Cl_2$.
Plumbic oxide,	$Pb''O$.
Plumbic tetrethide,	$Pb^{iv}Et_4$.
Plumbic peroxide,	$Pb^{iv}O_2$.
Diplumbic hexethide,	Pb'''_2Et_6.

History.—Lead has been known from the earliest historical times. The alchemists, who believed that a connection existed between the metals and the planets, designated lead *Saturn*, a name which is still preserved in the expression "saturnine poisoning," sometimes applied to poisoning by lead.

Occurrence.—Lead occurs widely distributed in nature. Native lead has been found in small quantities in volcanic tufa. The chief ore of

lead is the sulphide, or *galena*, PbS″. Other lead minerals are the carbonate or *cerussite*, COPbo″, and the sulphate or *anglesite*, SO_2Pbo''. It also occurs as phosphate, arsenate, chromate, and molybdate. England and Spain furnish the chief supply of lead. In England the most important mines are those of Cornwall and Cumberland.

Extraction.—Lead is chiefly obtained from galena. This ore is first roasted in a reverberatory furnace, by which treatment a portion of the sulphide is converted into oxide or sulphate. The temperature of the furnace is then raised, when the oxide and sulphate react with the unaltered sulphide, and a mutual reduction to metallic lead occurs, with evolution of sulphurous anhydride.

$$\underset{\text{Plumbic sulphide.}}{PbS''} + \underset{\text{Plumbic oxide.}}{2PbO} = 3Pb + \underset{\text{Sulphurous anhydride.}}{SO_2}.$$

$$PbS'' + \underset{\text{Plumbic sulphate.}}{SO_2Pbo''} = 2Pb + 2SO_2.$$

The above process can be employed only with ores of lead which are free from other metallic sulphides. In the case of ores containing pyrites, zinc-blende and other impurities, the *precipitation process* is employed. In this process the ore is reduced by fusion with cast iron, less of this metal being employed than is required to reduce the whole of the galena present. The iron combines with the sulphur to form ferrous sulphide, which rises to the surface with the other sulphides, whilst the molten lead sinks to the bottom of the furnace, and can be drawn off.

The lead obtained by either of the above processes always contains silver. This is profitably extracted by Pattinson's process of desilverization (p. 448). The oxide obtained in cupelling the portions of lead rich in silver is reduced by heating with carbon in a low blast-furnace.

Lead generally contains antimony, tin, and other impurities, the presence of which renders the metal hard. The process of removing these impurities, known as *softening* or *improving* the lead, consists in partially oxidizing it in a shallow cast-iron pan on the bed of a reverberatory furnace. The impurities are oxidized more readily than the lead, and pass into the layer of oxide which forms on the surface of the metal.

Properties.—Lead is a bluish-white metal, lustrous on the freshly cut surface. It is very soft and may be cut with a knife or scratched with the nail. It may be rolled into sheets of foil, but, owing to its want of tenacity, cannot be *drawn* into thin wire, though it may be formed into wire by *pressing* through a narrow opening. Lead contracts in solidifying, and objects cast in this metal frequently contain cavities. It may be obtained in regular octahedra by fusing a quantity of the metal, allowing it partially to solidify and then pouring off the liquid portion. It may also be obtained in the form of an aggregation of lustrous laminæ (lead-tree) by the electrolysis of solutions of its salts, or by suspending a piece of zinc or iron in such a solution. A clean and bright surface of lead speedily tarnishes on exposure to air, owing to oxidation. The fused metal becomes covered with a black film of sub-

oxide, which at a higher temperature is converted into yellow oxide. Pure water is without action upon lead as long as air is excluded, but in presence of air plumbic hydrate is formed, which is somewhat soluble in water. The presence of minute quantities of carbonates and phosphates in water greatly diminishes this solubility and prevents the corrosion of the lead. These facts are of great importance from a sanitary point of view, owing to the universal employment of lead pipes for conveying a supply of water, and the poisonous character of the compounds of lead. Fortunately almost all natural waters contain carbonates or phosphates, and the lead is thus protected from corrosion. Dihydric calcic dicarbonate—the solution of calcic carbonate in carbonic acid—an impurity present in most natural waters, is especially efficacious in this respect, causing a film of insoluble basic plumbic carbonate to be formed upon the surface of the lead. Basic plumbic carbonate, $CO(OPb''Ho)_2$ dissolves in pure water only to the extent of a sixtieth of a grain to the gallon: when a solution of plumbic hydrate in distilled water is exposed to the air carbonic anhydride is absorbed and the basic carbonate is deposited in silky crystals. Lead resists to a great extent the action of sulphuric and hydrochloric acids, but dissolves readily in nitric acid.

Uses.—The ease with which lead may be worked and its power of resisting the action of air, moisture, and acids, have led to its employment for various purposes: thus it is used for water-pipes, for roofing houses, and in the construction of sulphuric acid chambers. Rifle bullets and small shot are also made of this material, about 0.5 per cent. of arsenic being added in the latter case in order to aid the metal in assuming the spherical form. Various alloys of lead are also used in the arts. *Type metal* is an alloy of 2 parts of lead, 1 of antimony and 1 of tin. *Plumber's solder* is an alloy of lead and tin (p. 323).

COMPOUNDS OF LEAD WITH THE HALOGENS.

PLUMBIC CHLORIDE, $PbCl_2$. *Molecular volume* $\boxed{}\boxed{}$.—This compound has been found in the crater of Vesuvius as the mineral *cotunnite.* Hydrochloric acid attacks lead only very slowly, but hot aqua-regia dissolves it readily, depositing crystals of the chloride on cooling. It is best prepared by dissolving the oxide or the carbonate in hydrochloric acid. It is also precipitated as a crystalline powder when hydrochloric acid or a soluble chloride is added to a not too dilute solution of a lead salt.—Plumbic chloride crystallizes from water in long, colorless, lustrous prisms. It is soluble at ordinary temperatures in 130 parts, at 100° C. in less than 30 parts of water. When fused with exclusion of air, it solidifies on cooling to a white horn-like mass, but if air be admitted, it is converted into oxychloride. Oxychlorides of varying composition are obtained by fusing together plumbic oxide and plumbic chloride, or by precipitating a solution of plumbic chloride with an insufficiency of lime-water or ammonia. Those which are rich in chlorine are white; those which are rich in oxygen are yellow. Some of these compounds are employed as pigments. *Cassel yellow* is

an oxychloride obtained by heating plumbic oxide with ammonic chloride. · A white oxychloride, prepared by precipitating plumbic chloride with lime-water, is employed as a substitute for white lead.

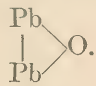
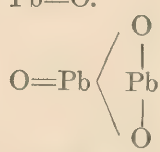
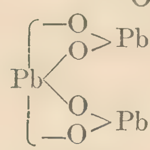
Plumbic perchloride, $\mathbf{Pb}Cl_4$, exists only in solution. When plumbic peroxide is dissolved in well-cooled concentrated hydrochloric acid, a strongly oxydizing liquid, which evolves chlorine on heating, is obtained.

Plumbic bromide, $\mathbf{Pb}Br_2$, resembles the chloride.

PLUMBIC IODIDE, $\mathbf{Pb}I_2$.—This compound is precipitated as a crystalline yellow powder when a soluble iodide is added to a solution of a lead salt. It is almost insoluble in cold, but dissolves slightly in hot water, yielding a colorless solution, which on cooling deposits the iodide in yellow laminæ. Plumbic iodide, when heated, becomes first red, then black, and finally fuses to a dark-colored liquid, which on cooling solidifies to a yellow crystalline mass. It dissolves in solutions of the alkaline iodides to form double salts.

Plumbic fluoride, $\mathbf{Pb}F_2$, is precipitated as a white almost insoluble powder, when hydrofluoric acid is added to the solution of a lead salt.

COMPOUNDS OF LEAD WITH OXYGEN.

Plumbous oxide, . . .	$\left\{\begin{matrix}\mathbf{Pb}\\ \mathbf{Pb}\end{matrix}\right.O.$	
Plumbic oxide, . . .	$\mathbf{Pb}O.$	Pb=O.
Diplumbic trioxide, . .	$\mathbf{Pb}O\mathbf{Pb}o''.$	
Triplumbic tetroxide, .	$\mathbf{Pb}\mathbf{Pb}o''_2.$	
Plumbic peroxide, . .	$\mathbf{Pb}O_2.$	O=Pb=O.

Plumbous oxide, $'\mathbf{Pb}'_2O$, is best prepared by heating plumbic oxalate to 300° C. with exclusion of air:

$$2\left\{\begin{matrix}CO\\ CO\end{matrix}\right.\mathbf{Pb}o'' = \left\{\begin{matrix}\mathbf{Pb}\\ \mathbf{Pb}\end{matrix}\right.O + 3CO_2 + CO.$$

Plumbic oxalate. Plumbous oxide. Carbonic anhydride. Carbonic oxide.

It is a black powder. When lead is fused in air, avoiding too high a temperature, the same compound is formed as a gray film on the surface of the metal. When heated to redness with exclusion of air, plumbous oxide is decomposed into plumbic oxide and metallic lead; if air is admitted, it burns like tinder and is totally converted into plumbic oxide. It slowly undergoes the same conversion when exposed to the air in a moist state. With acids it yields plumbic salts with separation of metallic lead.

Plumbic oxide (*Litharge*), PbO.—This compound is prepared by heating lead in air or by igniting plumbic carbonate or nitrate. It is obtained as a by-product in various metallurgical operations—notably in Pattinson's process for the desilverization of lead (p. 448)—Plumbic oxide is a yellow powder, which when strongly heated fuses, and on cooling solidifies to a yellow micaceous mass, sometimes with a shade of red. It is slightly soluble in water, to which it imparts an alkaline reaction. Acids dissolve it, forming the various salts of lead. Carbonic oxide at 100° C., and hydrogen at 310° C., reduce it to metallic lead. Plumbic oxide absorbs carbonic anhydride from the air.—Litharge is employed in the preparation of various salts and pigments of lead, in the manufacture of flint-glass, and in glazing earthenware.

Diplumbic oxydihydrate, Pb_2OHo_2, is precipitated when ammonia is added in excess to a solution of plumbic nitrate. Caustic alkalies may be substituted for ammonia, but in this case an excess of the precipitant must be avoided, as this would dissolve the plumbic hydrate. It is a white bulky precipitate, difficult to obtain free from basic salts. It is slightly soluble in water.—The hydrate $PbHo_2$ has not been prepared.

Diplumbic trioxide, $PbOPbo''$, is precipitated as a reddish-yellow powder, when sodic hypochlorite is carefully added to a solution of plumbic hydrate in caustic soda. It is decomposed at a red heat into plumbic oxide and oxygen. Hydrochloric acid dissolves it completely in the cold, yielding a yellow liquid, which speedily evolves chlorine and then contains plumbic chloride. Oxy-acids take up half the lead of this oxide to form plumbic salts, whilst the other half remains undissolved as plumbic peroxide.

Triplumbic tetroxide, $PbPbo''_2$.—This compound appears to be contained in *red-lead* or *minium*, which is, however, a substance of varying composition, intermediate between plumbic oxide and diplumbic trioxide. When finely divided litharge or plumbic carbonate is heated in air for twenty-four hours to dull redness, it is converted into a heavy scarlet crystalline powder. It becomes dark when heated, but recovers its original color on cooling. At a red-heat it is decomposed like the trioxide into plumbic oxide and oxygen. In its behavior towards acids it also resembles that compound.—Red-lead is employed as a pigment, also for electrical storage batteries, and in the manufacture of the finer sorts of flint-glass. For the latter purpose the excess of oxygen which it contains serves to effect the combustion of organic matters, and thus to prevent the reduction of the lead which would cause the glass to blacken.

Plumbic peroxide (*Puce-colored oxide of lead*), PbO_2, is most readily obtained by treating diplumbic trioxide or red-lead with nitric acid, when the peroxide remains as a dark-brown amorphous powder. The same compound is formed when chlorine is passed into an alkaline solution in which plumbic hydrate is suspended. It is also deposited on the positive electrode when the solution of a lead salt is electrolyzed. It occurs native in black six-sided prisms as *plattnerite*. At a red heat it is decomposed like the other higher oxides of lead into plumbic oxide and oxygen. When introduced into an atmosphere of sulphur-

ous anhydride, it is converted with incandescence into plumbic sulphate:

$$\underset{\text{Plumbic peroxide.}}{\mathbf{PbO_2}} + \underset{\text{Sulphurous anhydride.}}{\mathbf{SO_2}} = \underset{\text{Plumbic sulphate.}}{\mathbf{SO_2}\mathrm{Pbo}''}.$$

Sulphuric acid dissolves it with evolution of oxygen and formation of plumbic sulphate; hydrochloric acid dissolves it with evolution of chlorine and formation of plumbic chloride; nitric acid is without action upon it.—A porous mass of plumbic peroxide, generated by electrolysis, forms the negative plate in the Planté secondary battery and other electrical storage batteries constructed on the same principle (see p. 106).

OXY-SALTS OF LEAD.

Plumbic nitrate, $\left\{\begin{matrix}\mathbf{NO_2}\\ \mathrm{Pbo}''\\ \mathbf{NO_2}\end{matrix}\right.$, is best prepared by dissolving litharge in an excess of nitric acid and evaporating to the crystallizing point. The salt forms colorless octahedral crystals, soluble in twice their weight of cold water, much less soluble in water containing nitric acid. It is almost insoluble in alcohol. At a red heat it fuses and is decomposed into plumbic oxide, nitric peroxide, and oxygen. When thrown upon red-hot charcoal, it deflagrates. It is employed as a mordant in dyeing and calico-printing.—A boiling aqueous solution of plumbic nitrate dissolves plumbic oxide, and on cooling deposits acicular crystals of *plumbic nitrate hydrate*, $\mathbf{NO_3}(\mathrm{OPb''Ho})$. Other basic nitrates, of the formulæ $\mathbf{N_3O_3}\mathrm{Pbo''(OPb''Ho)_3}$ and $\mathbf{N}\mathrm{Pbo''_3(OPb''Ho)}$, are obtained by precipitating solutions of the normal nitrate with ammonia.

Plumbic nitrite, $\left\{\begin{matrix}\mathbf{NO}\\ \mathrm{Pbo}'',\mathbf{O}\mathrm{H_2}\\ \mathbf{NO}\end{matrix}\right.$.—This compound is most readily obtained by accurately precipitating argentic nitrite with plumbic chloride and evaporating the solution *in vacuo* over sulphuric acid. It forms soluble yellow prisms or laminæ. If the solution be boiled, nitrogen is evolved and a basic nitrite is formed. If a solution of plumbic nitrate in fifty times its weight of water be boiled with one and a half parts of lead for twelve hours, the liquid deposits on cooling flesh-colored needles of *diplumbic nitrite hydrate*, $\mathbf{N}\mathrm{Pbo''(OPb''Ho)}$. If carbonic anhydride be passed into the solution of this salt, three-fourths of the lead is precipitated as carbonate, and the liquid contains the normal nitrite. If a solution of plumbic nitrate be digested with metallic lead for a few hours at a temperature of 75° C. (167° F.), a yellow liquid is obtained, which on cooling deposits lustrous yellow tabular crystals of *dihydric diplumbic nitrate nitrite*, $\left\{\begin{matrix}\mathbf{N}\mathrm{Ho_2Pbo''}\\ \mathrm{Pbo''}\\ \mathbf{NO}\end{matrix}\right.$,—a salt formerly termed "basic hyponitrate of lead." Various other basic nitrites of lead have been prepared.

Plumbic carbonate, $\mathbf{CO}\mathrm{Pbo}''$, occurs native as the mineral *cerussite* in lustrous transparent rhombic crystals, isomorphous with those of arragonite. The same salt is obtained as a white crystalline precipitate by pouring a solution of plumbic nitrate into a solution of sesquicarbonate of ammonia. The carbonates of sodium and potassium cannot be employed for this purpose, as these precipitate mixtures

of basic plumbic carbonates, the composition of which varies with the concentration and the temperature. *White lead* is a basic carbonate of lead—*triplumbic dicarbonate dihydrate*, $\begin{matrix} CO(OPb''Ho) \\ CO(OPb''Ho) \end{matrix}\Big\} Pbo''$. It is manufactured on a large scale as a pigment by one or other of the following processes:

(1) *Dutch Process.*—This is the oldest process and yields the finest product, but the operations are somewhat tedious. Glazed earthenware pots are filled to a quarter of their depth with weak malt vinegar. In each pot, above the surface of the liquid and resting on a wooden support, a thin sheet of lead coiled into a spiral is placed vertically, or a series of cast gratings is put into the pot, and the pot is covered with a plate of lead. The pots are then embedded in spent tan-bark or horse-dung on the floor of a shed. The first layer of pots is then covered with boards, and a second layer, arranged like the first and also embedded in tan-bark or horse-dung, is built up over these, and so on till the shed is full. The pile generally reaches a height of from 18 to 20 feet, and contains about 12,000 pots with from 50 to 60 tons of lead. The action which takes place is as follows: The heat evolved by the fermentation of the bark or dung volatilizes the acetic acid in the vinegar, which gradually in presence of the oxygen of air, which for this purpose must have free access to the heap, converts the lead superficially into basic plumbic acetate:

$$\underset{\text{Acetic acid.}}{2\left\{\begin{matrix} CH_3 \\ COHO \end{matrix}\right.} + 2Pb + O_2 = \underset{\text{Plumbic acetate hydrate.}}{2\left\{\begin{matrix} CH_3 \\ CO(OPb''Ho) \end{matrix}\right.}.$$

The carbonic anhydride which is given off during the fermentation then acts upon the basic acetate, converting it into basic carbonate (white lead) and normal acetate:

$$\underset{\text{Plumbic acetate hydrate.}}{6\left\{\begin{matrix} CH_3 \\ CO(OPb''Ho) \end{matrix}\right.} + \underset{\text{Carbonic anhydride.}}{2CO_2} = \underset{\text{Triplumbic dicarbonate dihydrate.}}{\left.\begin{matrix} CO(OPb''Ho) \\ CO(OPb''Ho) \end{matrix}\right\} Pbo''}$$

$$+ \underset{\text{Plumbic acetate.}}{3\left\{\begin{matrix} CH_3 \\ CO \\ CO \\ CH_3 \end{matrix}\right. Pbo''} + \underset{\text{Water.}}{2OH_2}.$$

The normal acetate then reacts with a fresh portion of lead in presence of oxygen and water, and regenerates the basic acetate:

$$\underset{\text{Plumbic acetate.}}{\left\{\begin{matrix} CH_3 \\ CO \\ CO \\ CH_3 \end{matrix}\right. Pbo''} + Pb + O + \underset{\text{Water.}}{OH_2} = \underset{\text{Plumbic acetate hydrate.}}{2\left\{\begin{matrix} CH_3 \\ CO(OPb''Ho) \end{matrix}\right.}.$$

The basic acetate is again acted upon by the carbonic anhydride as above. In this way the process is theoretically continuous, and a small quantity of acetic acid ought to suffice for the conversion of an unlimited quantity of lead. In practice 100 lbs. of acetic acid are required to convert 50 tons of lead into white lead. At the end of from four to five weeks the conversion is nearly complete; the pile is taken to pieces and, on uncoiling the spirals, the white lead peels off in flakes from the unaltered lead if any of the latter is left. The crude product is ground while moist, and well washed to free it from acetate.

(2) *Thenard's Process.*—A solution of basic plumbic acetate of lead is first prepared by boiling sugar of lead with litharge. The basic carbonate is then precipitated from this solution by passing in carbonic anhydride. As a pigment, the product lacks opacity, and is consequently deficient in "body" or "covering power."

(3) *Milner's Process.*—In this process, which yields good results, an oxychloride of lead is converted into white lead by the action of gaseous carbonic anhydride. A mixture of litharge, common salt, and water is ground for some hours. Into the mixture of caustic soda and plumbic oxychloride thus obtained, carbonic anhydride is passed until the liquid is neutral. At this point the operation must be interrupted, otherwise the product will be spoiled.

White lead is a white amorphous powder. Its chief drawbacks are its poisonous character, and the fact that it is blackened by sulphuretted hydrogen.

PLUMBIC SULPHATE, SO_2Pbo'', occurs native as *anglesite* in transparent rhombic crystals. It is obtained as a heavy white crystalline precipitate when sulphuric acid or a soluble sulphate is added to the solution of a lead salt. The precipitate is almost insoluble in water, and still less soluble in dilute sulphuric acid; but concentrated sulphuric acid dissolves about 6 per cent. of its weight of the sulphate. It is also slightly soluble in dilute hydrochloric and in dilute nitric acid, whilst sodic thiosulphate and many ammonia salts, particularly the acetate and the tartrate, dissolve it readily. When plumbic sulphate is boiled with a solution of ammonic sulphate, the liquid deposits on cooling minute lustrous crystals of *plumbic diammonic disulphate* $\left\{\begin{array}{l}SO_2Amo\\Pbo''\\SO_2Amo\end{array}\right.$. Pure water decomposes this salt with separation of insoluble plumbic sulphate. By treating the normal salt with ammonia, *diplumbic sulphate,* $SOPbo''_2$, is obtained.

Plumbic dithionate, $\left\{\begin{array}{l}SO_2\\SO_2\end{array}\right.Pbo'',4OH_2$, or $\left\{\begin{array}{l}SHo_4\\SHo_4\end{array}\right.Pbo''$, is best prepared by neutralizing a solution of dithionic acid with plumbic carbonate. It forms large colorless hexagonal crystals, readily soluble in water.

PLUMBIC CHROMATES.—See Chromates.

Plumbic phosphates.—The *normal orthophosphate,* $P_2O_2Pbo''_3$, is obtained as a white amorphous precipitate when hydric disodic phosphate is added to a solution of an excess of plumbic acetate. It is insoluble in water and acetic acid, readily

soluble in nitric acid and caustic potash.—*Hydric plumbic phosphate*, $POHoPbo''$, is precipitated by free phosphoric acid from a solution of plumbic nitrate as a white crystalline powder.—A double phosphate and chloride of lead of the formula $P_3O_3Pbo''_4\left(\begin{smallmatrix}O\\Cl\end{smallmatrix}Pb''\right)$ occurs in nature in hexagonal crystals as the mineral *pyromorphite*. It is isomorphous with apatite (p. 357).

Plumbic arsenates.—These resemble the phosphates. A native double arsenate and chloride corresponding to pyromorphite is the mineral, *mimetesite*,

$$As_3O_3Pbo''_4\left(\begin{smallmatrix}O\\Cl\end{smallmatrix}Pb''\right),$$

which forms hexagonal crystals. Intermediate gradations between pyromorphite and mimetesite occur, in which the phosphorus and arsenic replace each other isomorphously.

Plumbic borates.—When the solution of a lead salt is precipitated with borax, *octohydric diplumbic hexaborate*, $B_6O_3Ho_8Pbo''_2$, is formed. When this is warmed with ammonia it is converted into a white powder of *dihydric plumbic diborate*, B_2OHo_2Pbo''.—By fusing together plumbic oxide and boric anhydride, a transparent vitreous mass (Faraday's heavy glass) is obtained, which possesses a much higher refractive power than flint-glass.

Plumbic silicate.—No definite silicate of lead has been prepared. When silica is fused with plumbic oxide a vitreous mass is obtained. Plumbic silicate is one of the constituents of flint-glass.

COMPOUND OF LEAD WITH SULPHUR.

PLUMBIC SULPHIDE, PbS''.—As the mineral *galena* this compound forms the principal ore of lead. It occurs in regular cubes with a bluish-gray color and a brilliant metallic lustre; also in crystalline masses. It possesses a very perfect cubical cleavage. The same compound is formed as a leaden-gray crystalline mass when lead is fused with sulphur, and as an amorphous black powder by precipitating a solution of lead salt with sulphuretted hydrogen. It fuses without decomposition at a bright red heat when air is excluded, and may even be sublimed in a current of hydrogen or carbonic anhydride. In this way it is obtained in small cubical crystals. When fused with access of air it is converted into plumbic sulphate. It dissolves in hot concentrated hydrochloric acid with evolution of sulphuretted hydrogen. Dilute nitric acid converts it into nitrate with separation of sulphur; the concentrated acid oxidizes it to sulphate.—When sulphuretted hydrogen, in quantity insufficient for complete precipitation, is passed into a solution of plumbic chloride, red and yellow sulpho-chlorides of varying composition separate out:

$$Cl—Pb—S—Pb—Cl,$$
$$\text{and } Cl—Pb—S—Pb—Pb—S—Pb—Cl.$$

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF LEAD.—The salts of lead are mostly colorless. They have a sweet, astringent, metallic taste, and are poisonous. When continually introduced in minute quantities into the system, the salts of lead act as a cumulative poison. The soluble normal salts with strong acid redden litmus; the basic salts, on the other hand, have an alkaline reaction. *Caustic alkalies* and *ammonia* precipitate white basic salts of lead, soluble in excess of caustic alkali, insoluble in ammonia. *Sulphuretted hydrogen* and *ammonic sulphide* produce a black precipitate of plumbic

sulphide, which is converted by fuming nitric acid into white insoluble plumbic sulphate, whilst dilute nitric acid converts it into soluble plumbic nitrate with separation of sulphur. *Sulphuric acid* and soluble *sulphates* precipitate plumbic sulphate, very sparingly soluble in water, still less soluble in dilute sulphuric acid, insoluble in alcohol, but soluble in solutions of various ammonium salts, such as the acetate and the tartrate. *Hydrochloric acid* and soluble *chlorides* yield with not too dilute solutions a white precipitate of plumbic chloride, soluble in hot water. *Potassic chromate* precipitates yellow plumbic chromate; *potassic iodide* yellow plumbic iodide. All compounds of lead, when heated with sodic carbonate or potassic cyanide upon charcoal in the reducing flame, yield a malleable bead of metallic lead. The lead compounds give a faint flame spectrum, containing lines in the green and a characteristic spark spectrum.

CHAPTER XL.

HEXAD ELEMENTS.

SECTION II.

URANIUM, U.

Atomic weight = 238.5. *Molecular weight unknown. Sp. gr.* 18.7. *Atomicity* ^{iv}, ^{vi}, *and* ^{viii} ?*; *also a pseudo-triad and a pseudo-pentad. Evidence of atomicity*:

Uranous chloride, ...	$U^{iv}Cl_4$.
Diuranous hexachloride, ...	$\left\{\begin{matrix} U'''Cl_3 \\ U'''Cl_3 \end{matrix}\right.$.
Uranic oxide, ...	$U^{vi}O_3$.
Diuranic decachloride, ...	$\left\{\begin{matrix} U^{v}Cl_5 \\ U^{v}Cl_5 \end{matrix}\right.$.

History.—Klaproth first pointed out in 1789 the existence of a new metal in the mineral pitchblende, and to this metal he gave the name uranium. The metal was isolated by Peligot in 1842.

Occurrence.—Uranium is of rare occurrence, and is never found native. Its chief ore is *pitchblende*, an impure uranous diuranate, $\begin{matrix} UO_2 \\ UO_2 \end{matrix} Uo^{iv}$. It also occurs as phosphate in *uranium mica*, and as carbonate in *liebigite*.

Preparation.—Metallic uranium is obtained by the action of sodium upon uranous chloride, UCl_4. The two substances are heated together in

* Uranium and molybdenum, which have been included in the hexadic group, appear to be capable of exercising octadic functions: thus in peruranic anhydride (UO_4) and molybdic persulphide (MoS_4).

a porcelain crucible with the addition of potassic chloride as a flux. The porcelain crucible is packed in powdered charcoal within a larger crucible. The whole is heated, at first to redness, afterwards to a higher temperature so as to fuse the uranium, which is thus obtained as a black regulus.

Properties.—Metallic uranium has a silvery lustre, but tarnishes by exposure to the air, becoming in course of time steel-blue, and ultimately black. It is hard and somewhat malleable. When heated in air it burns with scintillations, forming uranous diuranate. It does not decompose water even at its boiling-point. Acids readily dissolve it.

COMPOUNDS OF URANIUM WITH THE HALOGENS.

Diuranous hexachloride, $'U'''_2Cl_6$, is obtained in dark-brown needles by heating uranous chloride to redness in a current of hydrogen. It dissolves in water, yielding a purple solution, which rapidly absorbs oxygen from the air.

Uranous chloride, UCl_4, is prepared by heating a mixture of charcoal and any of the oxides of uranium in a current of dry chlorine. It is volatile at a red heat, and may be obtained by sublimation in dark-green octahedra, possessing a metallic lustre. It is very deliquescent, and hisses when thrown into water. Its solutions absorb oxygen from the air, and turn yellow.

Uranous bromide, UBr_4, and *uranous fluoride*, UF_4, have also been prepared.

Diuranic decachloride (*Uranic pentachloride*), $'U^v_2Cl_{10}$.—This compound is formed along with uranous chloride in the preparation of the latter compound, especially when the temperature is not permitted to rise too high. As it is more volatile than uranous chloride, it collects in a part of the tube further removed from the source of heat. If the current of chlorine be sufficiently slow, the decachloride forms black, needle-shaped crystals. The compound rapidly deliquesces on exposure to air. It begins to decompose at 120° C. into uranous chloride and free chlorine.

COMPOUNDS OF URANIUM WITH OXYGEN.

Uranous oxide, ...	UO_2.	$O{=}U{=}O.$
Uranic oxide (*uranic anhydride*), ...	UO_3.	$\begin{array}{c} O \\ \Vert \\ O{=}U{=}O. \end{array}$
Peruranic anhydride, . .	UO_4.	$\begin{array}{c} O \\ \Vert \\ O{=}U{=}O. \\ \Vert \\ O \end{array}$

The remaining oxides of uranium—$U_2O_5 = UOUo^{iv}$, *uranous uranate*, and $U_3O_8 = \begin{matrix}UO_2\\UO_2\end{matrix}Uo^{iv}$, *uranous diuranate*—are regarded as combinations of the two first oxides with each other.

Uranous oxide, UO_2.—This oxide remains when any of the higher oxides of uranium, or uranic oxalate, is heated in a current of hydrogen. It forms a brown powder, which when heated in air burns with formation of uranous diuranate. Strong acids dissolve it, yielding green solutions of uranous salts, from which alkalies precipitate dark-brown flocculent *uranous hydrate*, UHo_4.

Uranic oxide (*Uranic anhydride*), UO_3, is obtained as a brownish-yellow powder when uranic nitrate is heated in an oil bath to 250° C. until nitrous fumes cease to be evolved. At higher temperatures it parts with oxygen, and is converted into uranous diuranate. Uranic oxide acts both as a basic oxide and as the anhydride of an acid: thus, on the one hand, it combines with acids to form salts in which the dyad radical *uranyl* $(U^{vi}O_2)''$ plays the part of a dyad metal, and, on the other, it unites with alkalies to form the uranates (*q.v.*).—A *uranic hydrate* is also known, but is very difficult to obtain of constant composition.

Uranous diuranate (*Green oxide of uranium*), $\begin{matrix}UO_2\\UO_2\end{matrix}{}^2Uo^{iv}$, occurs native in an impure state as *pitchblende*. It is obtained as a green powder when uranous or uranic oxide, or ammonic uranate is gently heated in air. It is difficultly soluble in hydrochloric and sulphuric acids, readily soluble in nitric acid.

Uranous uranate (*Black oxide of uranium*), $UOUo^{iv}$, or $\left\{\begin{matrix}UO_2\\UO_2\end{matrix}\right.{}^2O$, is obtained as a black powder when any of the other oxides of uranium, or ammonic uranate, is strongly ignited in air. It is used in painting on porcelain.

OXY-HALOGEN COMPOUNDS OF URANIUM.

Uranylic chloride, UO_2Cl_2, is formed when uranous oxide is heated in a current of chlorine. It is a yellow, deliquescent, and very soluble mass, which is readily fusible, but volatilizes with some difficulty. It unites with the alkaline chlorides to form well-crystallized double salts: thus $UO_2Cl,2KCl_2,2OH_2$, and $UO_2Cl_2,2NH_4Cl,2OH_2$.

Uranylic bromide, UO_2Br_2, and *uranylic fluoride*, UO_2F_2, have also been prepared.

OXY-SALTS OF URANIUM.

a. Uranous Salts.

Uranous sulphate, $\begin{matrix}SO_2\\SO_2\end{matrix}{}^2Uo^{iv}$, occurs native, but partially oxidized to uranic sulphate as *uranium vitriol* or *johannite*. It is formed when uranous oxide is dissolved in sulphuric acid. The most convenient mode of preparing the salt consists in dissolving the green oxide in sulphuric acid, adding alcohol, and exposing the whole to sunlight. The liquid at first contains a mixture of a uranous and a uranic salt, but under the above conditions the uranic salt is reduced to the uranous stage, and the uranous sulphate, which is insoluble in dilute alcohol,

separates in crystals containing 4 aq. From aqueous solutions it crystallizes in green prismatic crystals with 8 aq. Excess of water decomposes it with separation of a green basic salt.

Uranous phosphate.—A *hydric uranous phosphate*, $P_2O_2Ho_2Uo^{iv},2OH_2$, is formed as a green gelatinous precipitate when hydric disodic phosphate is added to a solution of uranous chloride.

b. Uranic (Uranylic) Salts.

In the salts the dyad radical uranyl $(U^{vi}O_2)''$ plays the part of a dyad metal. They are characterized by possessing a yellow color with a magnificent green fluorescence.

Uranylic nitrate, $\begin{matrix} NO_2—O \\ NO_2—O \end{matrix}>U^{vi}O_2,6OH_2$, is obtained by dissolving any of the oxides in nitric acid and evaporating the solution. It crystallizes in large greenish-yellow rhombic prisms.

Uranylic sulphates.—The normal salt, $SO_2<\begin{matrix} O \\ O \end{matrix}>U^{vi}O_2,3OH_2$, is deposited in small lemon-yellow crystals when a solution of the nitrate is mixed with sulphuric acid and evaporated. A hot solution of this salt in moderately concentrated sulphuric acid deposits on cooling deliquescent, yellowish-green, fluorescent crystals of *hydric uranylic sulphate*, $\left\{\begin{matrix} SO_2Ho \\ O \\ UO_2 \\ O \\ SO_2Ho \end{matrix}\right.$. If, on the other hand, the normal salt be dissolved in fuming sulphuric acid, small yellow crystals of *uranylic pyrosulphate*, $\left\{\begin{matrix} SO_2—O \\ O \\ SO_2—O \end{matrix}\right.>U^{vi}O_2$, are obtained. These attract moisture with great avidity, and dissolve with a hissing noise when thrown into water. Uranylic sulphate forms double salts with the sulphates of the alkali metals; thus *potassic uranylic sulphate*,
$\left\{\begin{matrix} SO_2Ko \\ O \\ UO_2 \\ O \\ SO_2Ko \end{matrix}\right.,2OH_2$, forms yellow monoclinic crystals.

Phosphates and arsenates of uranyl occur native as rare minerals.

THE URANATES.

Besides behaving as a base towards acids, uranic oxide behaves towards strong bases as the anhydride of an acid, forming salts called *uranates*, in which the group uranyl $(UO_2)''$ plays the part of an acid radical. These salts are, however, not derived from a normal uranic acid of the formula UO_2Ho_2, corresponding to sulphuric acid, but from an anhydro-acid or *diuranic acid* of the formula $\left\{\begin{matrix} UO_2Ho \\ O \\ UO_2Ho \end{matrix}\right.$, corresponding to disulphuric or dichromic acid. Free diuranic acid has not been obtained.

Potassic uranate, $\left\{\begin{matrix}UO_2Ko\\ O\\ UO_2Ko\end{matrix}\right.$, is formed when uranic oxide is fused with an excess of potassic carbonate, and remains behind as a yellow powder when the mass is extracted with water.

Sodic uranate, $\left\{\begin{matrix}UO_2Nao\\ O\\ UO_2Nao\end{matrix}\right.$, is obtained in a similar manner by fusing uranic oxide with sodic carbonate. It is prepared on a large scale from pitchblende, and is employed under the name of *uranium yellow* in painting on porcelain and in the preparation of a beautiful greenish-yellow fluorescent glass.

Ammonic uranate, $\left\{\begin{matrix}UO_2(N^vH_4O)\\ O\\ UO_2(N^vH_4O)\end{matrix}\right.$, is formed as a yellow precipitate when ammonia is added to the solution of a uranyl salt. On heating, it is converted into pure uranous diuranate.

Bismuthous uranate hydrate, $\left\{\begin{matrix}UO_2(OBi'''Ho_2)\\ O\\ UO_2(OBi'''Ho_2)\end{matrix}\right.$, OH_2, or $UO_2Ho(OBi'''Ho_2)$, occurs native as *uranospherite* in brick-red hemispherical aggregations.

A series of *peruranates* has recently been obtained by the action of hydroxyl upon uranylic salts in alkaline solution. *Sodic peruranate*, $UO_2Nao_4,8OH_2$, forms golden-yellow needles. The peruranates are very unstable, and have not yet been thoroughly examined.

COMPOUNDS OF URANIUM WITH SULPHUR.

Uranous sulphide, US''_2.—This compound is obtained as a grayish-black amorphous powder by passing sulphuretted hydrogen over uranous chloride heated to redness. At a white heat a crystalline product is obtained. It is slowly decomposed in moist air with evolution of sulphuretted hydrogen. It is insoluble in dilute hydrochloric acid, but concentrated acids dissolve it readily.

Uranylic sulphide, UO_2S'', is a dark-brown precipitate obtained by adding ammonic sulphide to a solution of uranylic nitrate.

General Properties and Reactions of the Compounds of Uranium:

a. *Uranous Salts.*—The uranous salts are green. In solution they absorb oxygen from the air and are converted into uranic salts, whilst their color changes from green to yellow. *Caustic alkalies* and *ammonia* produce in their solutions a dark-brown flocculent precipitate of uranous hydrate. This absorbs oxygen and is converted into uranic hydrate, which at the same time combines with the base to form an insoluble uranate. *Sulphuretted hydrogen* gives no precipitate in acid solutions; *ammonic sulphide* precipitates a black sulphide.

b. *Uranic* (*Uranylic*) *Salts.*—The uranic salts are yellow. From their solutions *caustic alkalies* or *ammonia* precipitate a yellow insoluble uranate of the base. The *hydric carbonates* of the alkalies and *ammonic carbonate* precipitate yellow double carbonates of uranium with alkali or ammonium, which are readily soluble in an excess of the precipitant.

Sulphuretted hydrogen gives no precipitate in acid solution; *ammonic sulphide* precipitates dark-brown uranylic sulphide, readily soluble in dilute acids, even in acetic acid. *Potassic ferrocyanide* gives a reddish-brown precipitate.

The uranium compounds yield with borax and microcosmic salt beads which in the reducing flame are green, in the oxidizing flame yellow. The uranium compounds do not color the non-luminous flame.

MOLYBDENUM, Mo.

Atomic weight = 95.5. *Molecular weight unknown. Sp. gr.* 8.6. *Atomicity* $''$, ^{iv}, ^{vi}, and ^{viii}?* *Evidence of atomicity:*

Hypomolybdous chloride, ...	$Mo''Cl_2$.
Molybdous chloride, ...	$Mo^{iv}Cl_4$.
Molybdic anhydride, ...	$Mo^{vi}O_3$.

History.—Metallic molybdenum was first obtained by Hjehn in 1782.

Occurrence.—Molybdenum is of rare occurrence. It is found in combination with sulphur as *molybdenite*, MoS''_2; with oxygen in *molybdenum ochre* or native molybdic anhydride, MoO_3; and as plumbic molybdate, MoO_2Pbo'' in *wulfenite.* Many iron ores contain traces of molybdenum, which thus finds its way into the pig-iron.

Preparation.—Metallic molybdenum is obtained by heating molybdic anhydride or one of the chlorides to redness in a current of hydrogen. In the case of the oxide the reduction is always incomplete, and it is necessary to purify the product by heating in a current of dry gaseous hydrochloric acid, when the unattacked oxide volatilizes as *molybdic hydroxy-chloride*, $MoOHo_2Cl_2$.

Properties.—Pure molybdenum is a silver-white metal. It appears to be infusible at the highest temperature that can be artificially produced, but if it contains carbon it may be fused by the oxy-hydrogen flame. It is permanent in air at ordinary temperature, but, when heated in air, undergoes oxidation and is ultimately converted into molybdic anhydride. It is not attacked by dilute hydrochloric or sulphuric acid, but hot concentrated sulphuric acid dissolves it with a brown color. It is readily soluble in nitric acid and aqua-regia.

COMPOUNDS OF MOLYBDENUM WITH THE HALOGENS.

Hypomolybdous chloride, $MoCl_2$, is formed when dimolybdous hexachloride is heated in a current of dry carbonic anhydride:

$$'Mo'''_2Cl_6 = MoCl_2 + MoCl_4.$$

Dimolybdous hexachloride.	Hypomolybdous chloride.	Molybdous chloride.

The tetrachloride volatilizes, whilst hypomolybdous chloride remains as a yellow amorphous powder. Hypomolybdous chloride is stable

* See note, p. 614.

when exposed to air at ordinary temperatures, but is decomposed when heated in air. It is insoluble in water, but soluble in hydrochloric acid.

A *hypomolybdous bromide*, $\mathbf{Mo}Br_2$, has also been prepared.

Dimolybdous hexachloride, $'\mathbf{Mo}'''_2Cl_6$, is obtained as a reddish-brown powder, resembling in appearance amorphous phosphorus, when molybdic pentachloride is heated to 250° C. in a current of hydrogen. It is insoluble in water and in hydrochloric acid. When strongly heated, it yields a mixture of hypomolybdous chloride and molybdous chloride.

Dimolybdous hexabromide, $'\mathbf{Mo}'''_2Br_6$, is also known.

Molybdous chloride, $\mathbf{Mo}Cl_4$, is formed as above by heating the dimolybdous hexachloride. It is a brown crystalline powder, which when exposed to air deliquesces to a brown liquid. It may be volatilized with partial decomposition in a current of carbonic anhydride.

Molybdous iodide, $\mathbf{Mo}I_4$, is obtained by dissolving molybdous hydrate, $\mathbf{Mo}Ho_4$, in hydriodic acid and evaporating the solution.

Molybdic pentachloride, $\mathbf{Mo}Cl_5$. *Molecular volume* $\square\square$.—This compound is obtained by heating molybdenum or molybdous sulphide in a current of chlorine. It forms a lustrous, radio-crystalline mass, which fuses at 194° C. (481° F.) and boils at 268° C. (514° F.). It fumes on exposure to air, and gradually deliquesces. The molecular formula, $\mathbf{Mo}Cl_5$, as deduced from the vapor density of this compound, is abnormal, as this formula would necessitate the assumption either of pentadic molybdenum or of the presence of an odd number of free affinities in the molecule (see p. 179, footnote).

COMPOUNDS OF MOLYBDENUM WITH OXYGEN.

Hypomolybdous oxide, . . .	$\mathbf{Mo}O$.	
Dimolybdous trioxide, . . .	$\left\{\begin{matrix}\mathbf{Mo}O\\ \mathbf{Mo}O\end{matrix}\right.O.$	O O=Mo—Mo=O.
Molybdous oxide, ...	$\mathbf{Mo}O_2$.	O=Mo=O.
Molybdic anhydride, . .	$\mathbf{Mo}O_3$.	O ‖ O=Mo=O.

Hypomolybdous oxide, $\mathbf{Mo}O$, appears to be formed as a black powder by the action of hot caustic potash upon hypomolybdous chloride.

Dimolybdous trioxide, $'\mathbf{Mo}'''_2O_3$.—When dimolybdous hexachloride is decomposed with a caustic alkali, *dimolybdous hexahydrate*, $'\mathbf{Mo}'''_2Ho_6$, is obtained as a dark-brown powder, and this, when heated with exclusion of air, parts with water and is converted into dimolybdous trioxide. It forms a gray metallic powder, insoluble in acids.

Molybdous oxide, $\mathbf{Mo}O_2$.—This oxide is obtained, like the preceding, by heating the corresponding hydrate in absence of air. Thus prepared it forms a brown powder. When *sodic trimolybdate*, $\mathbf{Mo}_3O_8Nao_2$, is fused with a third of its weight of zinc, and the mass extracted with

water, molybdous oxide remains in the form of dark-blue prisms which appear violet-red by transmitted light. It is insoluble in water, hydrochloric acid, and caustic potash. Hot nitric acid oxidizes it to molybdic acid.—*Molybdous hydrate*, $\mathbf{Mo}Ho_4$, is obtained as a reddish-brown precipitate by treating molybdous chloride with ammonia.

Molybdic anhydride, $\mathbf{Mo}O_3$.—This compound is most readily prepared by roasting the native sulphide, $\mathbf{Mo}S_2$, in air. After the sulphur has burnt off, the impure molybdic anhydride is extracted with ammonia, and the ammonium salt thus obtained is purified by crystallization. The ammonium salt may be converted into the anhydride either by heating it in small portions with free access of air, or by decomposing it with nitric acid, evaporating to dryness, and washing the residue thoroughly with water, when the anhydride remains undissolved. It forms a white powder which turns yellow on heating, but becomes white again on cooling. It fuses at a red heat, and may be sublimed in lustrous laminæ. It is insoluble in water and acids, but dissolves readily in caustic alkalies and ammonia.

Molybdic acid, $\mathbf{Mo}O_2Ho_2$, separates as a white crystalline powder from the solution of a molybdate to which hydrochloric or nitric acid has been added. The compound is insoluble in water, but dissolves in an excess of acid. From hot solutions a molybdic acid of the formula $\mathbf{Mo}_5O_{14}Ho_2$ is deposited. A soluble colloidal modification of molybdic acid is obtained by dissolving sodic molybdate in hydrochloric acid and subjecting the solution to dialysis; a yellow acid liquid remains, which yields on evaporation a gummy deliquescent mass. When a solution of molybdic acid in hydrochloric acid is treated with zinc the liquid becomes first blue, then green, and finally brown, owing to the formation of various molybdous and hypomolybdous molybdates.

Numerous *oxy-halogen* compounds of molybdenum have been prepared. They are generally volatile, and are mostly decomposed by water. The following list contains some of the compounds of this class:

Molybdic oxytetrachloride, ...	$\mathbf{Mo}OCl_4$.
Molybdic dioxydichloride, ...	$\mathbf{Mo}O_2Cl_2$.
Molybdic dioxydibromide, ...	$\mathbf{Mo}O_2Br_2$.
Dimolybdic trioxy-hexachloride, . . .	$\left\{\begin{array}{l}\mathbf{Mo}OCl_3\\ O\\ \mathbf{Mo}OCl_3\end{array}\right.$.

THE MOLYBDATES.

The salts of molybdic acid may be divided into the following classes:

Normal molybdates, ...	$\mathbf{Mo}O_2Ro_2$.
Dimolybdates, ...	$\mathbf{Mo}_2O_5Ro_2$.
Trimolybdates, ...	$\mathbf{Mo}_2O_8Ro_2$.
Tetramolybdates, ...	$\mathbf{Mo}_4O_{11}Ro_2$.
Heptamolybdates, ...	$\mathbf{Mo}_7O_{12}Ro_6$.
Octomolybdates, ...	$\mathbf{Mo}_8O_{23}Ro_2$.
Decamolybdates, ...	$\mathbf{Mo}_{10}O_{29}Ro_2$.

in which R stands for a monad metal.

All these salts, with the exception of the heptamolybdates, are derived from dibasic acids.

Potassic molybdates.—The normal salt, MoO_2Ko_2, is obtained by fusing together equal molecular proportions of potassic carbonate and molybdic anhydride, dissolving the mass in water, and evaporating the filtered solution over sulphuric acid. It forms small soluble deliquescent crystals.—The dimolybdate has not been obtained.—The *trimolybdate*, $Mo_3O_8Ko_2,3OH_2$, is prepared like the normal salt, employing the requisite proportions of anhydride and carbonate. It crystallizes in flexible silky needles.—Other potassic molybdates have been obtained.

Sodic molybdates.—These are prepared like the potassium salts. Normal *sodic molybdate*, $MoO_2Nao_2,2OH_2$, forms nacreous laminæ or acute rhombohedra; *sodic dimolybdate*, $Mo_2O_5Nao_2$, small silky needles; *sodic trimolybdate*, $Mo_3O_8Nao_2,7OH_2$, very fine, sparingly soluble needles. Sodic molybdates corresponding to all the various classes in the above list have been prepared.

Of the other molybdates, those of barium, strontium, and calcium are either only sparingly soluble or insoluble in water, the magnesium and zinc salts are soluble and crystallize well. Normal *plumbic molybdate*, MoO_2Pbo'', occurs native in yellow quadratic crystals as *wulfenite*.

Phosphomolybdic Acid.

Molybdic acid forms with phosphoric acid a remarkable compound hexabasic acid, which may be regarded as a combination of 2 molecules of phosphoric acid with 22 molecules of molybdic anhydride. Both this acid and its salts contain large and varying proportions of so-called water of crystallization, which is very possibly present as water of constitution. Owing to the complexity of these salts and the absence of all certain knowledge with regard to their constitution, it will be simplest to formulate them as molecular combinations.

Phosphomolybdic acid, $2POHo_3,22MoO_3$.—This compound is obtained by boiling ammonic phosphomolybdate with aqua-regia, and allowing the solution to evaporate spontaneously. From this solution it crystallizes in yellow triclinic prisms with 20 aq., from pure water in cubes with 50 aq., and from concentrated nitric acid in rhombic crystals with 40 aq.

Ammonic phosphomolybdate, $2POAmo_3,22MoO_3,12OH_2$, is precipitated as a yellow crystalline powder when orthophosphoric acid or a soluble orthophosphate is added to an excess of a solution of ammonic molybdate in nitric acid. It is insoluble in water and in dilute acids. In solutions containing an excess of phosphoric acid no precipitate is formed.

Potassic phosphomolybdate, $2POKo_3,22MoO_3,12OH_2$, is obtained in minute four-sided prisms by boiling the ammonium salt with caustic potash, or by precipitating a potash salt with a solution of phosphomolybdic acid.

A second series of phosphomolybdates derived from an acid of the formula $2POHo_3,5MoO_3$, is obtained by spontaneous evaporation of a solution of the above salts in excess of alkali or ammonia. Thus from an ammoniacal solution of the yellow precipitate of ammonic phosphomolybdate in ammonia, lustrous prisms of a salt, $2POAmo_3,5MoO_3,7OH_3$, are deposited.

COMPOUNDS OF MOLYBDENUM WITH SULPHUR.

MOLYBDOUS SULPHIDE, MoS''_2, occurs native as *molybdenite* in lead-gray hexagonal crystals, or in masses closely resembling graphite in appearance, with which it was formerly confounded. It is obtained as a lustrous powder when molybdic anhydride is heated in a current of sulphuretted hydrogen :

$$\underset{\text{Molybdic anhydride.}}{MoO_3} + \underset{\text{Sulphuretted hydrogen.}}{3SH_2} = \underset{\text{Molybdous sulphide.}}{MoS''_2} + S + \underset{\text{Water.}}{3OH_2}.$$

The trisulphide, when heated with exclusion of air, is also converted with evolution of sulphur into the disulphide. When heated in air, molybdous sulphide is oxidized to molybdic anhydride and sulphurous anhydride.

Molybdic sulphide (*Molybdic sulphanhydride*), MoS''_3, is precipitated when hydrochloric acid is added to the solution of a molybdate previously saturated with sulphuretted hydrogen. It is a dark-brown powder which dissolves in solutions of alkaline sulphides, forming sulphomolybdates. *Potassic sulphomolybdate*, MoS''_2Ks_2, forms prismatic crystals, which by reflected light appear green with a metallic lustre, and by transmitted light ruby-red.

Molybdic persulphide, MoS''_4.—When a solution of potassic molybdate is saturated with sulphuretted hydrogen and then boiled, a mixture of molybdous sulphide with molybdic sulphide is precipitated, and the solution contains *potassic persulphomolybdate*, MoS''_3Ks_2, which crystallizes in small, transparent, red scales. On adding hydrochloric acid to the solution of this salt molybdic persulphide, MoS''_4, is precipitated as a reddish-brown powder.

GENERAL PROPERTIES AND REACTIONS OF THE COMPOUNDS OF MOLYBDENUM.—The *hypomolybdous* and *molybdous* salts are of relatively slight importance. The *molybdates* and *molybdic acid* give characteristic reactions with reducing agents. Thus, if metallic zinc be added to a dilute hydrochloric acid solution of a molybdate, the liquid becomes blue, then green, and finally dark-brown. *Sulphuretted hydrogen* first colors the acid solution blue, and then precipitates molybdic sulphide; but the whole of the molybdenum can be precipitated only by repeated treatment with sulphuretted hydrogen, allowing the solution to stand in a warm place. *Potassic ferrocyanide* gives a reddish-brown precipitate. The compounds of molybdenum yield, with borax and with microcosmic salt, beads which in the oxidizing flame are colorless or pale yellow; in the reducing flame the borax bead is brown, and the bead of microcosmic salt green.

TUNGSTEN, W.

Atomic weight = 184. *Molecular weight unknown. Sp. gr.* 19.129. *Atomicity* $''$, ^{iv}, *and* ^{vi}. *Evidence of atomicity :*

Hypotungstous chloride, ...	$W''Cl_2$.
Tungstous chloride, ...	$W^{iv}Cl_4$.
Tungstic hexachloride, ...	$W^{vi}Cl_6$.

History.—Tungstic acid was first obtained by Scheele from the mineral scheelite in 1781.

Occurrence.—Tungsten occurs only in combination, and almost invariably in the form of tungstates. *Wolfram* is a tungstate of iron and manganese; *schcelite* is a calcic tungstate, WO_2Cao''; and *scheelitine* is a plumbic tungstate, WO_2Pbo''. Tungstic anhydride, WO_3, occurs as the rare mineral *wolfram ochre*.

Preparation.—Metallic tungsten is prepared by the reduction of the oxides or chlorides in a current of hydrogen. The reduction of the chlorides may also be effected by means of sodium, and that of the oxides by carbon. The metal has not been obtained in the coherent state.

Properties.—Tungsten forms a lustrous metallic powder, which, when the reduction has been effected at a white heat, consists of minute quadratic plates. It is unalterable in air at ordinary temperatures, but when heated to redness in air is converted into tungstic anhydride. Nitric acid oxidizes it slowly, aqua-regia rapidly, to tungstic acid.

The quality of steel is stated to be improved by the addition of tungsten.

COMPOUNDS OF TUNGSTEN WITH THE HALOGENS.

Hypotungstous chloride, WCl_2, is most readily obtained by heating the tetrachloride in a current of carbonic anhydride (see Tungstous chloride). It forms a gray non-volatile powder, which is decomposed by exposure to the air. In contact with water it slowly evolves hydrogen, and is converted into brown hydrated dioxide, whilst the liquid contains hydrochloric acid.

Hypotungstous bromide, WBr_2, and *hypotungstous iodide*, WI_2, have also been prepared.

Tungstous chloride, WCl_4, is formed during the preparation of the pentachloride from the hexachloride. As it is non-volatile, it remains behind in the process of sublimation. It forms a yellowish-brown infusible crystalline mass. When strongly heated with exclusion of air it splits up into tungstic pentachloride, which volatilizes, and hypotungstous chloride, which remains:

$$\underset{\text{Tungstous chloride.}}{3WCl_4} = \underset{\text{Tungstic pentachloride.}}{2WCl_5} + \underset{\text{Hypotungstous chloride.}}{WCl_2}.$$

It is hygroscopic, and is decomposed by water into hydrochloric acid and brown hydrated tungstous oxide.

TUNGSTIC PENTACHLORIDE, WCl_5. *Molecular volume* $\square\square$.—This compound may be obtained by careful distillation of the hexachloride in a current of hydrogen. It is best, however, to carry the reduction as far as the formation of the tetrachloride, which may be done by employing a higher temperature, and then to decompose the tetrachloride by heating still more strongly in a current of carbonic anhydride, when it breaks up into pentachloride and dichloride (see Tungstous chloride). It forms black lustrous needles, fusing at 248° C. (478° F.) and boiling

at 275.6° C. (528° F.). The vapor is yellowish-green. (As regards the anomalous molecular weight of this compound, as deduced from the vapor density, see p. 179, footnote.) It is very hygroscopic, and is decomposed by water with separation of a blue compound supposed to be a tungstous tungstate.

TUNGSTIC HEXACHLORIDE, WCl_6. *Molecular volume* □□.—When tungsten is heated in a current of chlorine, combination occurs with incandescence, and the hexachloride is formed. The metal employed must be perfectly free from oxide, and the chlorine must contain neither air nor moisture, otherwise the product will be contaminated with oxytetrachloride, $WOCl_4$. It forms a violet-black crystalline mass, fusing at 275° C. (527° F.) and boiling at 346.7° C. (654° F.). In the neighborhood of its boiling-point the vapor possesses a density corresponding with the formula WCl_6; at higher temperatures the density is less, owing to dissociation. Pure tungstic hexachloride is not altered by exposure to air, but when it contains oxychloride it undergoes decomposition, evolving fumes of hydrochloric acid. In like manner the pure hexachloride is not decomposed by water until heated with it, but that which contains oxychloride is at once decomposed in the cold with formation of a greenish oxide. It is soluble in carbonic disulphide, yielding a reddish-brown solution, from which it is deposited in brown six-sided plates.

COMPOUNDS OF TUNGSTEN WITH OXYGEN.

Tungstous oxide, WO_2, is obtained when tungstic anhydride is heated to low redness in a current of hydrogen. Too high a temperature must be avoided, as otherwise metallic tungsten will be formed. On the other hand, if too low a temperature be employed, tungstous tungstate, $WO_2(O_2W^{iv}O)''$, is obtained as a blue powder. Tungstous oxide is a brown powder, which is scarcely attacked by acids. When freshly prepared it is pyrophoric, and must be allowed to remain for some time in an atmosphere of hydrogen before exposing it to the air.

TUNGSTIC ANHYDRIDE, WO_3, occurs native as the rare mineral *wolfram ochre*. It is best obtained from *wolfram*, a tungstate of manganese and iron. The finely powdered mineral is digested for several days on the water-bath with hydrochloric acid, and finally with aqua-regia. The insoluble portion, which consists of tungstic acid along with unattacked wolfram and gangue, is washed with water and extracted with ammonia, which dissolves the tungstic acid. The ammonic tungstate is converted into the anhydride by ignition.—Tungstic anhydride is a yellow powder, which is fusible at a very high temperature, and may be volatilized at a white heat. Exposure to light colors it green. It may be obtained in greenish crystals by fusion with borax, or by igniting a mixture of sodic carbonate and sodic tungstate in a current of gaseous hydrochloric acid. It dissolves in caustic soda and caustic potash, but is insoluble in ammonia and in acids.

TUNGSTIC ACID.—This acid exists in several modifications. When an acid is added to a cold solution of a tungstate, a white precipitate is obtained, which when dried by exposure to air possesses the composition

$\mathbf{W}OHo_4$. When this compound is dried over sulphuric acid it parts with water, and is converted without change of color into the dibasic acid, $\mathbf{W}O_2Ho_2$. The latter compound may also be obtained as a yellow precipitate by pouring the hot solution of a tungstate into hot nitric acid, or by boiling an insoluble tungstate with nitric acid. These acids are insoluble in water. In contact with zinc and hydrochloric acid, tungstic acid is colored first blue and afterwards brown, owing to the formation of tungstous tungstate and of a lower oxide—probably the hydrated dioxide.—A soluble *metatungstic acid*, $\mathbf{W}_4O_{11}Ho_2,7\mathbf{O}H_2$, is obtained by decomposing baric metatungstate (see Tungstates) with sulphuric acid, or plumbic metatungstate with sulphuretted hydrogen, and evaporating at ordinary temperature. It forms soluble yellow octahedra. The solution has an acid reaction, and may be concentrated to a syrup, but on boiling the concentrated solution a separation of ordinary insoluble tungstic acid occurs.—A second soluble modification, *colloidal tungstic acid*, is obtained like the corresponding modification of molybdic acid (p. 621) by adding to a 5 per cent. solution of sodic tungstate a quantity of hydrochloric acid sufficient to combine with the sodium, and subjecting the liquid to dialysis. The solution may be boiled either alone or with acids without depositing ordinary tungstic acid. The colloidal acid may be obtained by evaporation as a vitreous mass, which may be heated to 200° C. (392° F.) without being converted into the insoluble modification. The vitreous acid dissolves slowly but completely in one-fourth of its weight of water. When strongly heated, all the modifications of tungstic acid are converted into the anhydride.

As in the case of molybdenum, oxy-halogen compounds of tungsten have been prepared:

Tungstic oxytetrachloride, ...	$\mathbf{W}OCl_4$.
Tungstic dioxydichloride, ...	$\mathbf{W}O_2Cl_2$.
Tungstic dioxydibromide, ...	$\mathbf{W}O_2Br_2$.

THE TUNGSTATES.

Tungstic acid forms a series of very complex salts.. These resemble in many respects the salts of molybdic acid, especially in the case of the *polytungstates*, which correspond with the polymolybdates, and are formed by the combination of the normal salt with the anhydride in varying proportions. The complexity is further increased by the existence of a separate class of salts, the *metatungstates*, which are distinguished by not yielding a precipitate on the addition of an acid, except after prolonged boiling.

Potassic tungstates.—The normal salt is obtained by adding tungstic anhydride in small quantities at a time to fused potassic carbonate, dissolving the cooled mass in hot water. The solution deposits on cooling prismatic crystals of the formula $\mathbf{W}O_2Ko_2 2,\mathbf{O}H_2$. When a solution of the normal salt is boiled with tungstic anhydride as long as the latter dissolves, a *duodecatungstate* of the formula $\mathbf{W}_{12}O_{31}Ko_{10},11\mathbf{O}H_2$ separates in lustrous scales as the liquid cools.

Sodic tungstates.—The normal salt, $\mathbf{W}O_2Nao_2,2\mathbf{O}H_2$, is obtained like

the potassium salt, and crystallizes in thin rhombic prisms. The following is a list of the sodic tungstates which have been prepared:

Disodic ditungstate, ...	$WO_2Nao_22OH_2$.
Disodic ditungstate, ...	$W_2O_5Nao_2,2OH_2$.
Tetrasodic tritungstate, . .	$W_3O_7Nao_4,7OH_2$.
Tetrasodic pentatungstate, .	$W_5O_{13}Nao_4,11OH_2$.
Hexasodic heptatungstate, .	$W_7O_{18}Nao_616OH_2$, or $21OH_2$.
Decasodic dodecatungstate, .	$W_{12}O_{31}Nao_{10},21OH_2$, or $25OH_2$,or $28OH_2$.

The dodecatungstate, also known as *sodic paratungstate,* is manufactured by roasting the mineral wolfram with soda ash and extracting the fused mass with water. The solution is almost neutralized with hydrochloric acid and then left to crystallize. At ordinary temperatures the aquate with 28 aq. is deposited in large triclinic crystals; at higher temperatures the other aquates given in the above list are obtained. This salt is sometimes employed as a mordant, and also in rendering cotton and linen fabrics uninflammable.—*Sodic metatungstate,* $W_4O_{11}Nao_2$,-$10OH_2$, is obtained by boiling normal sodic tungstate with tungstic anhydride. It crystallizes in efflorescent octahedra, which are soluble in less than one-tenth of their weight of cold water.

Ammonic tungstates.—The normal salt has not been prepared, but various polytungstates and a metatungstate are known.

The following tungstates occur as minerals:

Calcic tungstate (*scheelite*), ...	WO_2Cao''.
Plumbic tungstate (*stolzite*), ...	WO_2Pbo''.
Ferrous tungstate (*farberite*), ...	WO_2Feo''.
Manganous tungstate (*hübnerite*)	WO_2Mno''.

An isomorphous mixture of the last two compounds constitutes the mineral *wolfram.*

A class of *phospho-tungstates* is known, corresponding with the phosphomolybdates.

Silico-tungstic Acids.—Some of the polytungstic acids combine with silicic acid to form peculiar compound acids. When sodic or potassic heptatungstate is boiled with gelatinous silicic acid, salts of *silico-dodecatungstic acid,* $SiW_{12}O_{34}Ho_8$, are formed. In order to obtain the free acid, mercurous nitrate is added to the solution of the salts, and the precipitate of mercurous silicotungstate, after washing, is decomposed with hydrochloric acid. The filtrate from the mercurous chloride deposits on spontaneous evaporation large, colorless, lustrous, quadratic octahedra of the above acid with 29 aq. When heated it fuses in its water of crystallization and deposits at a temperature of 53° C. rhombohedra containing 22 aq. It forms both normal and acid salts: thus the three potassic silicotungstates have had the following formulæ assigned to them:

$$SiW_{12}O_{34}Ko_8,14OH_2,$$
$$SiW_{12}O_{39}Ho_4Ko_4,15OH_2,$$
$$2SiW_{12}O_{34}Ho_5Ko_3,25OH_2.$$

If gelatinous silicic acid be boiled with an ammonic polytungstate, the ammonium salts of two other silicotungstic acids are formed: of a *silicodecatungstic acid,* $SiW_{10}O_{28}Ho_8$, $3OH_2$, and of a silico-dodecatungstic acid isomeric with that above described. This second dodeca-acid is known as *tungsto-silicic acid.* It crystallizes in triclinic prisms with 20 aq., and its salts are distinguished from those of ordinary silico-tungstic acid by greater solubility, by crystallizing in different forms, and by containing a different number of molecules of water of crystallization.

The Tungsto-tungstates.

These compounds, which may be regarded as combinations of the tungstates with

tungstous oxide, are obtained by the reduction of the polytungstates. They are characterized by metallic lustre, and have been employed as bronze powders.

Potassic tungsto-tungstate, $\left\{\begin{array}{l} WO_2Ko \\ O \\ WO \\ O \\ WO_2Ko \end{array}\right.$.—Tungstic anhydride is added to fused potassic tungstate as long as it dissolves. The mass thus obtained is then reduced by gently heating in a current of hydrogen, and is then extracted successively with water, hydrochloric acid, caustic potash, and again with water. It is thus obtained in dark-blue needles, with a coppery lustre.

Sodic tungsto-tungstate, $W_3O_7Nao_2$, may be obtained either by a method similar to the above, or by fusing a polytungstate of sodium with tin, and extracting the mass with caustic soda and hydrochloric acid. It crystallizes in golden cubes, with a fine metallic lustre.

COMPOUNDS OF TUNGSTEN WITH SULPHUR.

Tungstous sulphide, WS_2'', is formed when the trisulphide is heated with exclusion of air, or when tungstic anhydride is heated in a current of sulphuretted hydrogen:

$$\underset{\text{Tungstic anhydride.}}{WO_3} + \underset{\text{Sulphuretted hydrogen.}}{3SH_2} = \underset{\text{Tungstous sulphide.}}{WS''_2} + S + \underset{\text{Water.}}{3OH_2}.$$

It forms a blue-black crystalline powder.

Tungstic sulphide (*Tungstic sulphanhydride*), WS''_3, is obtained like the corresponding molybdenum compound by saturating the solution of a tungstate with sulphuretted hydrogen and then adding an acid. It is a dark-brown powder, which dissolves in alkaline sulphides with formation of sulpho-tungstates. *Potassic sulphotungstate,* WS''_2Ks_2, forms yellow prismatic crystals.

General Properties and Reactions of the Compounds of Tungsten.—The insoluble compounds of tungsten can be obtained in a soluble form as alkaline tungstates by fusion with an alkali, preferably with the addition of nitre. When metallic *zinc* or *tin* is introduced into the hydrochloric acid solution of a tungstate, the liquid assumes a deep-blue color. *Ammonic sulphide* produces in the solution of a tungstate no precipitate, but if hydrochloric acid be added to the liquid thus obtained, tungstic sulphide is precipitated as a dark-brown powder. The tungsten compounds yield with microcosmic salt a bead which, in the oxidizing flame, is colorless or pale yellow, in the reducing flame blue. On the addition of ferrous sulphate, the bead assumes a blood-red color in the reducing flame.

CHAPTER XLI.

HEXAD ELEMENTS.

SECTION III.

CHROMIUM, Cr.

Atomic weight = 52. *Molecular weight unknown. Sp. gr.* 7.3 (Bunsen). *Atomicity* $''$, ^{iv}, ^{vi}, *and possibly* ^{viii}; *also a pseudo-triad. Evidence of atomicity:*

Chromous chloride, ...	$\mathbf{Cr}''Cl_2$.
Chromic chloride, ...	$\left\{\begin{array}{l}\mathbf{Cr}'''Cl_3\\ \mathbf{Cr}'''Cl_3.\end{array}\right.$
Chromic perfluoride, ...	$\mathbf{Cr}^{vi}F_6$.
Chromic anhydride, ...	$\mathbf{Cr}^{vi}O_3$.
Perchromic acid, ...	$\left\{\begin{array}{l}\mathbf{Cr}^{vii}O_3Ho(?).\\ \mathbf{Cr}^{vii}O_3Ho\end{array}\right.$

History.—Chromium was discovered by Vanquelin in 1797, and independently by Klaproth about the same time.

Occurrence.—Chromium does not occur abundantly, and is never found in the free state. Its chief natural compounds are those which it forms with other metals, together with oxygen. Of these the most abundant is *chrome iron ore*, $'\mathbf{Cr}_2O_2Feo''$. It also occurs as plumbic chromate, $\mathbf{Cr}O_2Pbo''$, *crocoisite*. The color of various minerals and gems, such as serpentine, chromic mica, and the emerald, is due to the presence of small quantities of chromium.

Preparation.—Chromium may be reduced from its chloride by means of zinc. For this purpose the chloride is heated with zinc in a Hessian crucible, employing a mixture of potassic chloride and sodic chloride as a flux. The zinc regulus is treated first with cold and afterwards with warm dilute nitric acid, as long as anything dissolves. The metallic chromium remains as a gray powder. For the above reaction, it is not necessary to prepare anhydrous chromic chloride: the mixture of chromic chloride and potassic chloride obtained by the reduction of potassic dichromate with hydrochloric acid and alcohol is evaporated with the addition of sodic chloride, and the mass thus obtained is carefully dried and employed as above.—Chromium may also be obtained by heating chromic oxide to a very high temperature with sugar in a lime crucible.—Bunsen has prepared the metal by the electrolysis of a solution of chromous chloride containing chromic chloride.

Properties.—Metallic chromium, reduced from the chloride by zinc, is a light-gray crystalline powder, in which, by the aid of the microscope, tin-white lustrous octahedra may be perceived. Prepared by electrolysis, it is deposited on a platinum electrode as a coherent plate. It is more difficultly fusible than platinum, and as hard as corundum. It is only slowly oxidized when heated in air with a Bunsen or hydrogen flame, but burns with brilliant scintillations in the oxy-hydrogen flame.

When thrown on potassic chlorate which has been heated to incipient fusion, it is oxidized with dazzling incandescence, yielding potassic chromate. Hydrochloric acid dissolves it readily with evolution of hydrogen; dilute sulphuric acid scarcely attacks it in the cold, but when hot dissolves it, also evolving hydrogen; nitric acid, even when hot and concentrated, does not act upon it. The hardness of steel is greatly increased by the addition of 0.5 to 0.75 per cent. of chromium.

COMPOUNDS OF CHROMIUM WITH THE HALOGENS.

a. Chromous Compounds.

Chromous chlorides, $CrCl_2$.—A solution of this compound is obtained when the metal is dissolved in hydrochloric acid. The anhydrous chloride is best prepared by gently heating chromic chloride in a current of dry hydrogen. It forms a white crystalline mass, and dissolves in water, yielding a blue solution, which rapidly absorbs oxygen from the air and possesses powerful reducing properties.

Chromous bromide, $CrBr_2$, is prepared in a similar manner from chromic bromide. It resembles the chloride in its properties.

b. Chromic Compounds.

CHROMIC CHLORIDE, $'Cr_2Cl_6$, is prepared by heating a mixture of chromic oxide and carbon in a current of dry chlorine. It forms lustrous scales, of the color of peach-blossom, which may be sublimed in a current of chlorine. When heated in air, it evolves chlorine and is converted into chromic oxide. Pure chromic chloride is almost insoluble in water at ordinary temperatures, and dissolves only slowly when boiled with water for a considerable time, but in presence of a very minute quantity of chromous chloride, it dissolves readily in cold water, yielding a green liquid. Stannous chloride and other reducing agents produce the same effect. The green solution, which may also be obtained by dissolving chromic hydrate in hydrochloric acid, yields, by evaporation over sulphuric acid, green, very soluble needles of the compound $'Cr_2Cl_6,12OH_2$. These, when heated, part with water and hydrochloric acid, and are converted into an oxychloride. By heating in a current of gaseous hydrochloric acid, they may, however, be converted into the anhydrous violet chloride.

Chromic bromide, $'Cr_2Br_6$, is prepared like the chloride. It forms black hexagonal scales, with a submetallic lustre. The crystals exhibit, by transmitted light, olive-green and red dichroism.

Chromic fluoride, $'Cr_2F_6$, is obtained by dissolving chromic hydrate in hydrofluoric acid. On evaporating the solution a green crystalline mass is obtained, which fuses at a red heat, and at a very high temperature sublimes in lustrous regular octahedra.

c. Perchromic Compounds.

Only one of these is known—the *perfluoride*. In all circumstances where the formation of a perchloride or perbromide might be expected, chlorine or bromine is evolved, and the corresponding chromic compound is formed.

Chromic perfluoride, CrF_6, is prepared by heating a mixture of calcic fluoride and ignited plumbic chromate with concentrated sulphuric acid in a retort of lead or platinum:

$$\underset{\text{Plumbic chromate.}}{CrO_2Pbo''} + \underset{\text{Calcic fluoride.}}{3CaF_2} + \underset{\text{Sulphuric acid.}}{4SO_2Ho_2} = \underset{\text{Chromic fluoride.}}{CrF_6} +$$

$$\underset{\text{Plumbic sulphate.}}{SO_2Pbo''} + \underset{\text{Calcic sulphate.}}{3SO_2Cao''} + \underset{\text{Water.}}{4OH_2}.$$

A red gas passes over, which condenses to a red fuming liquid. In contact with water it is decomposed, yielding chromic and hydrofluoric acids.

COMPOUNDS OF CHROMIUM WITH OXYGEN.

Chromic oxide, ... $\left\{\begin{matrix} CrO \\ CrO \end{matrix}\right\}O$. O=Cr—Cr=O (with O bridging the two Cr above).

Chromic anhydride, . . CrO_3. O=Cr=O (with O double-bonded to Cr above).

Chromous oxide, CrO, is not known, but its hydrate and several of its salts have been prepared.—*Chromous hydrate*, $CrHo_2$, is obtained as a brownish-yellow precipitate by the addition of caustic potash to a solution of chromous chloride. It readily absorbs oxygen, and must be dried with exclusion of air. When heated in absence of air, it parts with water and hydrogen, being converted into chromic oxide:

$$\underset{\text{Chromous hydrate.}}{2CrHo_2} = \underset{\text{Chromic oxide.}}{Cr_2O_3} + \underset{\text{Water.}}{OH_2} + H_2.$$

Chromic oxide, $'CrO_{23}$.—This oxide occurs native as the mineral *chrome-ochre*, contaminated with earthy impurities. It is formed when chromic hydrate, chromic anhydride, or diammonic dichromate, is heated:

$$\underset{\text{Diammonic dichromate.}}{\left\{\begin{matrix} CrO_2(NH_4O) \\ O \\ CrO_2(NH_4O) \end{matrix}\right.} = \underset{\text{Chromic oxide.}}{\left\{\begin{matrix} CrO \\ CrO \end{matrix}\right\}O} + N_2 + \underset{\text{Water.}}{4OH_2}.$$

It is most readily obtained by heating a mixture of equal parts of dipotassic dichromate and sulphur, or of dipotassic dichromate and ammonic chloride. On extracting the residue with water, the chromic oxide remains undissolved. It is a dark-green amorphous powder, which fuses in the oxy-hydrogen flame, and solidifies to an almost black, crystalline mass. It may be obtained in lustrous, dark-green, hexagonal crystals by passing the vapor of chromic oxydichloride, CrO_2Cl_2, through a red-hot tube. The strongly ignited oxide is almost insoluble in acids.

Chromic oxide is used as a pigment under the name of *chrome green*, and in the preparation of green glass and enamel.

CHROMIC HYDRATE, $'\mathbf{Cr}_2Ho_6$.—Ammonia produces in solutions of chromic salts free from alkali a pale-blue precipitate of a hydrate which, after drying over sulphuric acid, has the formula $'\mathbf{Cr}_2Ho_6,4\mathbf{O}H_2$. In a vacuum it slowly parts with 3 aq., and when heated to 220° C. in a current of hydrogen is converted into the hydrate $'\mathbf{Cr}_2O_2Ho_2$. Another hydrate of the formula $'\mathbf{Cr}_2OHo_4$, employed as a pigment under the name of *Guignet's green*, is prepared by fusing dipotassic dichromate with boric acid, and extracting the mass with water. These hydrates are difficultly soluble in acids. Freshly precipitated chromic hydrate dissolves slightly in aqueous ammonia, yielding a peach-blossom-colored solution. This solubility depends upon the formation of a chromamine corresponding with the cobaltamines (*q.v.*). The freshly precipitated hydrate also dissolves in a solution of chromic chloride, and from the solution thus obtained the greater part of the hydrochloric acid may be removed by dialysis, leaving a soluble colloidal modification of chromic hydrate. (Graham found in the liquid remaining in the dialyser 1 mol. of hydrochloric acid to 33 mols. of chromic hydrate). The dark-green solution is not precipitated by dilution or by boiling, but the addition of the slightest trace of a salt causes it to coagulate.—The precipitate produced in solutions of chromic salts by caustic alkalies, which dissolves in an excess of the precipitant, and is reprecipitated by boiling, always contains alkali; and this cannot be removed by washing.

CHROMIC ANHYDRIDE, $\mathbf{Cr}O_3$.—In order to prepare this compound, $1\frac{1}{2}$ volumes of concentrated sulphuric acid are added to one volume of a cold saturated solution of dipotassic dichromate. On cooling, the chromic anhydride crystallizes out in long red needles. It may be freed from the excess of acid by allowing it to drain upon a porous tile, in which condition it is sufficiently pure for most purposes. In order to obtain it quite pure, the crystals must be filtered off, employing a filter of asbestos or spun glass, as organic substances instantly reduce the anhydride, and the substance must be washed upon the filter with pure nitric acid free from nitrous anhydride, and finally freed from the nitric acid by warming in a current of dry air.—Chromic anhydride forms either a woolly mass of fine red needles, or red prisms. It is very soluble in water, yielding a reddish-brown solution, which becomes yellow on dilution. It is also soluble both in concentrated and in dilute sulphuric acid, but it is almost insoluble in a sulphuric acid containing from 16 to 17 per cent. of water—a property which is utilized in its preparation. It fuses without decomposition when heated, but at 250° C. (482° F.) is resolved into chromic oxide and oxygen. It is very readily reduced to chromic oxide, and therefore acts as a powerful oxidizing agent. Sulphurous anhydride, sulphuretted hydrogen, nitrous anhydride, and most organic substances effect its reduction. Alcohol poured upon the dry anhydride inflames. Glacial acetic acid, however, dissolves it without decomposition. Both the aqueous and the acetic acid solutions of chromic anhydride are employed in organic chemistry as oxidizing agents, the latter solution being particularly efficacious, owing to the fact that the acetic acid generally also acts as a solvent for the organic substance which is to be oxidized. Sometimes, instead of

aqueous chromic anhydride, a solution of dipotassic dichromate in dilute sulphuric acid is employed as an oxidizing agent. When heated with hydrochloric acid, chromic anhydride evolves chlorine, and is converted into chromic chloride; heated with concentrated sulphuric acid it gives off oxygen, yielding chromic sulphate.

CHROMIC ACID, CrO_2Ho_2. See Chromates.

Perchromic acid, $\left\{\begin{array}{l}CrO_3Ho \\ CrO_3Ho\end{array}\right.$(?).—When hydroxyl is added to a solution of chromic anhydride or of a chromate acidified with sulphuric acid, a deep-blue coloration is produced. The compound thus formed, which is possibly a perchromic acid of the above composition, speedily decomposes with evolution of oxygen, and the solution contains only chromic acid. On agitating the blue solution with ether, this solvent extracts the blue compound from the water, and rises to the surface as a dark-blue layer. The ethereal solution, though somewhat more stable than the aqueous solution, leaves only chromic anhydride on evaporation. The formation of this blue compound is a very delicate and characteristic test, both for chromic anhydride and for hydroxyl—indeed, for the latter substance it is the only thoroughly characteristic test.

The other oxides of chromium generally enumerated are difficult to obtain of constant composition. A *chromous dichromic tetroxide*, $'Cr_2O'Cro''$, is probably formed in the process of preparing the metal by electrolysis, but appears to be mixed with metallic chromium. The substance known as *chromic dioxide*, CrO_2, is probably a compound of chromic anhydride with chromic oxide; by washing with water it is decomposed into these two substances.

OXY-SALTS OF CHROMIUM.

a. Chromous Salts.

The chromous salts are of slight importance. They are readily oxidizable, and absorb oxygen from the air.

Chromous sulphate, SO_2Cro'', is known only in solution. It is formed when metallic chromium is dissolved in dilute sulphuric acid. *Dipotassic chromous sulphate*, $\left\{\begin{array}{l}SO_2Ko \\ Cro'' \\ SO_2Ko\end{array}\right.$, $6OH_2$, is prepared by dissolving potassic sulphate in a solution of chromous chloride, adding alcohol, and then allowing the mixture to stand for some time with exclusion of air. It crystallizes in blue monoclinic prisms, which on exposure to air quickly become green from oxidation.

Chromous phosphate, $P_2O_2Cro''_3$, and *chromous carbonate*, $COCro''$, have also been prepared.

b. Chromous Salts.

Chromic oxide forms with acids the chromic salts, in which the hexadic group $('Cr'''_2)^{vi}$ displaces six atoms of hydrogen in the acid. The aqueous solutions, prepared by dissolving the salts in cold water, are violet colored; on heating, the color changes to green, and on cooling, the violet color returns only after a considerable time. Crystallized salts can be obtained only from the violet solutions: the green solutions yield, by evaporation or on the addition of alcohol, green amorphous masses. The violet solutions alone contain a pure chromic salt; this, on warming, is decomposed into basic salt and free acid, the chemical change being accompanied by the above change of color.

Chromic nitrate, $\mathbf{N}_6O_{12}('Cr'''_2O_6)^{vi},18\mathbf{O}H_2$, is prepared by dissolving chromic hydrate in nitric acid. It forms red, soluble, monoclinic crystals.

CHROMIC SULPHATE, $\mathbf{S}_3O_6('Cr'''_2O_6)^{vi},15\mathbf{O}H_2$, is prepared by dissolving chromic hydrate in its own weight of concentrated sulphuric acid. The solution, which is green at first, becomes blue on standing, and deposits a violet-blue crystalline mass of the above salt. This may be purified by dissolving in cold water and precipitating with alcohol. From its solution in cold dilute alcohol it is deposited in blue regular octahedra. The aqueous solution prepared in the cold has a violet color, which changes to green on boiling.

DIPOTASSIC CHROMIC SULPHATE (*Chrome alum*),

$$\left.\begin{array}{l}\mathbf{S}O_2Ko-\\ \mathbf{S}O_2-\\ \mathbf{S}O_2-\\ \mathbf{S}O_2Ko-\end{array}\right]('Cr'''_2O_6)^{vi},24\mathbf{O}H_2.$$

—This compound is best prepared by dissolving equal molecular proportions of dipotassic dichromate and sulphuric acid in water and passing sulphurous anhydride into the solution:

$$\left\{\begin{array}{l}\mathbf{Cr}O_2Ko\\ O\\ \mathbf{Cr}O_2Ko\end{array}\right. + \mathbf{S}O_2Ho_2 + 3\mathbf{S}O_2 = \left.\begin{array}{l}\mathbf{S}O_2Ko-\\ \mathbf{S}O_2-\\ \mathbf{S}O_2-\\ \mathbf{S}O_2Ko-\end{array}\right]('Cr'''_2O_6)^{vi} + \mathbf{O}H_2.$$

Dipotassic dichromate.	Sulphuric acid.	Sulphurous anhydride.	Chrome alum.	Water.

Other reducing agents, such as alcohol, may be employed instead of sulphurous anhydride, but in this case it is necessary to add a larger quantity of sulphuric acid. Chrome alum crystallizes in deep ruby-red octahedra, which by reflected light appear almost black. It dissolves in cold water with a reddish-violet color, which becomes green on boiling. After standing for a long time it recovers its original color. Chrome alum is employed in dyeing and calico-printing, and in tanning. —*Ammonia chrome alum* is prepared like the potassium compound, which it closely resembles in its properties.

THE CHROMITES.

Chromic oxide possesses the property of combining with other oxides—especially with the oxides of the dyad metals—to form compounds which may be regarded as salts of the acid $'\mathbf{Cr}_2O_2Ho_2$. To this particular hydrate of chromium the name *chromous acid* may therefore be applied, and these compounds would then be termed *chromites*. It has already been mentioned that when chromic hydrate is precipitated by caustic alkalies, the precipitate contains alkali which cannot be removed by washing. This is due to the formation of a chromite of the alkali. Only the chromites of the dyad metals, however, have been obtained as well characterized compounds. These crystallize in regular octahedra, and belong to the same class as the aluminates of the dyad metals (p. 568), or as magnetic oxide of iron (*q.v.*), all of which also crystallize in regular octahedra, and may be regarded as formed by the combination of a monoxide with a sesquioxide.

Zincic chromite, $'Cr_2O_2Zno''$, is obtained in lustrous blackish-green octahedra by fusing a mixture of zincic oxide and chromic oxide with boric anhydride.

Manganous chromite, $'Cr_2O_2Mno''$, is obtained in a similar manner, substituting manganous oxide for zincic oxide. It forms very hard iron-gray octahedra.

FERROUS CHROMITE, $'Cr_2O_2Feo''$, occurs in nature as the mineral *chrome iron ore.* It generally occurs in crystalline masses; but distinct octahedral crystals are also found.

THE CHROMATES.

These are the salts of the unknown chromic acid, CrO_2Ho_2. This acid possibly exists in the aqueous solution of chromic anhydride, but on evaporating this solution only chromic anhydride is obtained. Hydroxyl does not appear to be capable of entering into stable combination with the radical chromyl $(CrO_2)''$. Not only does chromic acid part spontaneously with the elements of water to yield an anhydride; but not even the acid chromates are capable of existing. Thus in all cases in which the formation of *hydric potassic chromate* might be expected, two molecules of this salt combine, with elimination of one molecule of water, anhydro-salt *dipotassic dichromate,* $\left\{\begin{array}{l} CrO_2Ko \\ O \\ CrO_2Ko \end{array}\right.$.

When chromic oxide, a chromic salt, or any substance containing chromium is fused with nitre, the chromium is oxidized by the oxygen of the nitre, and a yellow mass is obtained which contains potassic chromate, CrO_2Ko_2. Formerly this compound was prepared by heating chrome iron ore with nitre, but at the present day potashes are substituted for the more costly nitre, and the oxidation is effected by means of the oxygen of the air. Chrome iron ore is first roasted and then finely ground. A mixture of roasted and powdered ore, crude potashes, and lime is first dried at 150° C. (302° F.) and then heated to bright redness in the oxidizing flame of a reverberatory furnace. The addition of the lime prevents the fusion of the mass, which is thus kept in a pasty condition. During the operation the heated mass is constantly stirred, so as to expose fresh surfaces to the oxidizing action of the flame. As soon as the oxidation is complete the charge is withdrawn, and, after cooling, is lixiviated with the smallest possible quantity of boiling water. If the solution should contain calcic chromate, potassic sulphate is added in quantity sufficient to convert it into the potassium salt, the calcium being at the same time precipitated as sulphate. The solution now contains potassic chromate, but it would be impossible to separate this salt by crystallization from the other salts present, owing to its ready solubility. It is therefore necessary to convert it into the less soluble dichromate. For this purpose a quantity of sulphuric acid sufficient to saturate half the potassium present as chromate is diluted with twice its volume of water and added to the solution:

$$\underset{\text{Potassic chromate.}}{2CrO_2Ko_2} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Dipotassic dichromate.}}{\left\{\begin{array}{l} CrO_2Ko \\ O \\ CrO_2Ko \end{array}\right.} + \underset{\text{Potassic sulphate.}}{SO_2Ko_2} + \underset{\text{Water.}}{OH_2}.$$

The normal chromate is soluble in twice its weight of cold water, whilst the dichromate requires ten times its weight of water for solution; the greater part of the dichromate therefore crystallizes from the above liquid on cooling. The mother liquor, which contains potassic sulphate, is employed in the extraction of another roasted charge. The potassic dichromate is purified by crystallization. (For the properties of this salt see below.)

POTASSIC CHROMATE, CrO_2Ko_2.—(For the mode of formation, see preceding paragraph.) In order to obtain this salt in a state of purity an excess of caustic potash is added to a solution of the dichromate. The color of the solution changes from orange-red to yellow, and on evaporation yellow rhombic crystals of the normal chromate are deposited. The crystals are isomorphous with those of potassic sulphate, with which salt it is capable of crystallizing in all proportions. It is soluble in twice its weight of cold water, yielding a yellow solution. It has an alkaline reaction. The pure salt undergoes decomposition when its solutions are evaporated: crystals of the dichromate are first deposited; afterwards when the solution begins to contain more free alkali, the normal salt crystallizes out. Acids, even carbonic, decompose it with formation of dichromate. On heating, it turns red and fuses at a high temperature without decomposition, recovering its original color on cooling.

Dipotassic dichromate, $\left\{\begin{array}{l} CrO_2Ko \\ O \\ CrO_2Ko \end{array}\right.$.—(For the mode of preparation, see p. 635.) This salt crystallizes in large garnet-red triclinic prisms or tabular crystals. It is soluble in 10 parts of water at ordinary temperatures, more readily soluble in boiling water. The solution has an acid reaction. The salt fuses below a red heat without decomposition, but at a white heat is decomposed into normal chromate, chromic oxide and oxygen. When heated with concentrated sulphuric acid it evolves oxygen and yields a green solution which, after dilution with water, deposits on standing crystals of chrome alum. It is a violent poison.—Dipotassic dichromate is the starting point in the preparation of the other chromium compounds. It is employed as a laboratory reagent, as an oxidizing agent, in dyeing and calico-printing, and in the process of producing permanent carbon photographs.

Dipotassic trichromate, $\left\{\begin{array}{l} CrO_2Ko \\ O \\ CrO_2 \\ O \\ CrO_2Ko \end{array}\right.$, and *Dipotassic tetrachromate,* $Cr_4O_{11}Ko_2$, are deposited from solutions of the foregoing salt in nitric acid. They form deep-red crystals, which are decomposed by water into dichromate and chromic anhydride.

Sodic chromate, CrO_2Nao_2, is obtained when a solution of potassic chromate with an excess of caustic soda is evaporated at 0°. It crystallizes at a low temperature in large yellow transparent deliquescent prisms of the formula $CrO_2Noa_2,10OH_2$, isomorphous with crystallized sodic sulphate, from warm solutions in anhydrous crystals.—*Disodic dichromate,* $Cr_2O_5Nao_2,2OH_2$, forms deliquescent red prisms.

Ammonic chromate, $\mathbf{Cr}O_2(N^vH_4O)_2$, and *diammonic dichromate*, $\mathbf{Cr}_2O_5(N^vH_2O)_2$, are obtained by adding the requisite quantity of ammonia to an aqueous solution of chromic anhydride. They resemble in almost every respect the corresponding potash salts. When heated they are decomposed into nitrogen, water, and chromic oxide—the normal salt also evolving ammonia. In the case of the dichromate, this decomposition is attended with incandescence, and the chromic oxide swells up to a bulky mass resembling green tea in appearance.

BARIC CHROMATE, $\mathbf{Cr}O_2Bao''$, is obtained as a yellow crystalline precipitate when the solution of a chromate or dichromate is added to the solution of a barium salt. It is insoluble in water and in acetic acid, soluble in hydrochloric and in nitric acid. It also dissolves in a hot aqueous solution of chromic anhydride, and the liquid deposits on cooling red crystals of *baric dichromate*, $\mathbf{Cr}_2O_5Bao'',2\mathbf{O}H_2$. These are decomposed by water into chromic anhydride and normal chromate.—Baric chromate constitutes the pigment *yellow ultramarine*.

Strontic chromate, $\mathbf{Cr}O_2Sro''$, closely resembles the barium salt, but is much more readily soluble in water and in acetic acid.

Calcic chromate, $\mathbf{Cr}O_2Cao'',2\mathbf{O}H_2$, is obtained in large yellow prismatic crystals by digesting marble with a solution of chromic anhydride and evaporating the liquid over sulphuric acid.

Magnesic chromate, $\mathbf{Cr}O_2Mgo'',7\mathbf{O}H_2$, forms soluble lemon-yellow rhombic crystals, and is isomorphous with magnesic sulphate.

Dipotassic magnesic chromate, $\left\{\begin{matrix}\mathbf{Cr}O_2Ko\\ Mgo''\\ \mathbf{Cr}O_2Ko\end{matrix}\right.,2\mathbf{O}H_2$, is deposited in yellow tabular crystals when a solution of dipotassic dichromate is neutralized with magnesia and then evaporated. *Diammonic magnesic chromate*, $\left\{\begin{matrix}\mathbf{Cr}O_2(N^vH_4O)\\ Mgo\\ \mathbf{Cr}O_2(N^vH_4O)\end{matrix}\right.,6\mathbf{O}H_2$, is isomorphous with diammonic magnesic sulphate (p. 511).

Zincic chromates.—The normal salt is not known, but various basic chromates of zinc have been prepared. *Dizincic chromate dihydrate*, $\mathbf{Cr}O_2(OZn''Ho)_2,\mathbf{O}H_2$, is obtained as a yellow precipitate when normal potassic chromate is added to a solution of an excess of zincic sulphate.

PLUMBIC CHROMATE, $\mathbf{Cr}O_2Pbo''$, occurs native as *crocoisite* in red monoclinic crystals. The same substance is obtained as a bright yellow precipitate when potassic chromate or dichromate is added to the solution of a lead salt. This precipitate is employed as a pigment under the name of *chrome yellow*. It is insoluble in water and acetic acid, but soluble in nitric acid and in caustic potash. When heated it fuses without decomposition, and solidifies to a crystalline mass. Organic compounds, when heated with it, undergo complete oxidation: it is therefore employed in the ultimate analysis of such compounds, particularly of those which contain sulphur and chlorine or the metals of the alkalies and alkaline earths.—Chrome yellow is employed in calico-printing. The cloth is first mordanted with the solution of a lead salt. On afterward immersing it in a solution of potassic chromate, the chrome yellow is developed on the fibre of the mordanted parts.—*Diplumbic chromate*, $\mathbf{Cr}OPbo''_2$, a basic salt, constitutes the *chrome red* of commerce. It is formed as a red powder by boiling chrome yellow with normal potassic chromate, or by digesting it with cold caustic soda. It is also obtained as a vermilion-colored crystalline powder by

fusing chrome yellow with nitre. *Chrome orange* is a mixture of chrome red and chrome yellow. It is prepared by precipitating the solution of a lead salt with a weak alkaline solution of potassic chromate.

ARGENTIC CHROMATE, $\mathbf{Cr}O_2Ago_2$, is formed as a red crystalline precipitate when a dilute solution of normal potassic chromate is added to a concentrated solution of argentic nitrate. It may be obtained in dark-green crystals by boiling diargentic dichromate with water, or by allowing a solution of the dichromate in ammonia to evaporate. The green crystals yield a red powder. It is insoluble in water, but dissolves in nitric acid, in ammonia, and in solutions of the alkaline chromates.—*Diargentic dichromate*, $\mathbf{Cr}_2O_5Ago_2$, is obtained as a scarlet precipitate when a solution of potassic dichromate is gradually added to a solution of argentic nitrate. When hot dilute solutions are employed the salt gradually separates in red triclinic crystals.

Mercuric chromate, $\mathbf{Cr}O_2\mathbf{Hg}o''$.—The normal salt is obtained in garnet-red rhombic prisms by boiling mercuric oxide with a solution of chromic anhydride. Excess of water decomposes it with separation of the red amorphous basic salt, *trimercuric chromate*, $\mathbf{Cr}Hgo''_3$,—a decomposition which exactly corresponds with that which occurs when normal mercuric sulphate is treated with water (p. 535). Potassic chromate produces in solutions of mercuric and mercurous salts precipitates of basic chromates of mercury.

COMPOUNDS OF CHROMIUM WITH OXYGEN AND CHLORINE.

CHROMIC OXYDICHLORIDE (*Chromylic chloride*, $\mathbf{Cr}O_2Cl_2$), *Molecular volume* $\square\square$.—This compound may be theoretically derived from chromic acid by the substitution of chlorine for hydroxyl. It may therefore be regarded as the chloride of the acid radical chromyl $(CrO_2)''$, and bears the same relation to chromic acid that sulphurylic chloride, $\mathbf{S}O_2Cl_2$, does to sulphuric acid. In order to prepare this compound, a fused mixture of 10 parts of common salt and 12 parts of dipotassic dichromate is broken into small pieces and introduced into a retort, after which 30 parts of faintly fuming sulphuric acid are introduced. The reaction begins of its own accord. The dark reddish-brown vapors are condensed in a cooled receiver. In order to free the product from dissolved chlorine, it must be repeatedly rectified in a current of dry carbonic anhydride. The same compound is formed when a dry mixture of chromic anhydride and ferric chloride is distilled.—Chromic oxydichloride is a mobile liquid, which appears almost black by reflected light, but exhibits a blood-red color by transmitted light. It boils at 128° C. (244° F.). It possesses a specific gravity of 1.92 at 25° C. (77° F.). In contact with moist air it fumes strongly, and when dropped into water is decomposed with violent ebullition, yielding chromic and hydrochloric acids. It has a most energetic action upon oxidizable substances: thus it acts upon phosphorus with explosive violence, whilst sulphur, sulphuretted hydrogen, ammonia, and many organic bodies, such as alcohol, inflame when brought in contact with it.

Chromic oxychlorhydrate (*Chromylic chlorhydrate*, *Chlorochromic acid*), $\mathbf{Cr}O_2ClHo$, a compound corresponding with sulphuric oxychlorhydrate

(SO_2ClHo), has, like chromic acid itself, not been isolated. The non-existence of this compound is a further instance of the inability of the semimolecule of hydroxyl to attach itself to the radical chromyl (see p. 638). Salts of chromic oxychlorhydrate, known as *chlorochromates*, have, however, been prepared. *Potassic chlorochromate* is obtained by gently warming 3 parts of dipotassic dichromate with 4 parts of concentrated hydrochloric acid and a little water:

$$\left\{\begin{array}{l} \mathbf{Cr}O_2Ko \\ O \\ \mathbf{Cr}O_2Ko \end{array}\right. + 2HCl = 2\mathbf{Cr}O_2ClKo + \mathbf{O}H_2.$$

Dipotassic dichromate. Hydrochloric acid. Potassic chlorochromate. Water.

It crystallizes in large red prisms or tables having a specific gravity of 2.497. An excess of pure water decomposes it into potassic chloride and chromic anhydride; but it may be recrystallized from dilute hydrochloric acid. When heated at 100° C. it evolves chlorine.

COMPOUND OF CHROMIUM WITH SULPHUR.

Chromic sulphide, $\left\{\begin{array}{l} \mathbf{Cr}S'' \\ \mathbf{Cr}S'' \end{array}\right\}S''$, is obtained by the direct union of its elements under the influence of heat. It is also formed when chromic oxide is heated to whiteness in the vapor of carbonic disulphide, or when chromic chloride is heated in a current of sulphuretted hydrogen.—Chromic sulphide is a gray-black powder with a metallic lustre. It possesses a specific gravity of 3.77. Concentrated nitric acid is without action upon it. When heated in air it is converted into chromic oxide.—Sulphuretted hydrogen produces no precipitate in solutions of chromic salts, and alkaline sulphides precipitate chromic hydrate with liberation of sulphuretted hydrogen.

COMPOUND OF CHROMIUM WITH NITROGEN.

Chromic nitride, $\left\{\begin{array}{l} \mathbf{Cr}N''' \\ \mathbf{Cr}N''' \end{array}\right.$, is formed by the direct union of its elements when nitrogen is passed over metallic chromium at a red heat; also by the action of gaseous ammonia upon heated chromide chloride.—It forms a heavy black powder which inflames when heated to 200° C. (392° F.) in contact with air. Heated with exclusion of air to a temperature higher than that at which it is formed, it is decomposed into its elements. Chlorine is without action upon it at ordinary temperatures, but when the substance is heated in a current of chlorine it is converted with a series of slight explosions into chromic chloride and free nitrogen. The explosions are due to the formation and immediate decomposition of nitrous chloride. It may be ignited without change in hydrogen and in steam. It is not attacked by hydrochloric or nitric acid, or by aqueous caustic potash. Concentrated sulphuric acid dissolves it, yielding a green liquid which, when diluted with water and allowed to stand, deposits crystals of ammonia chrome alum:

$$\left\{\begin{array}{l} \mathbf{Cr}N''' \\ \mathbf{Cr}N''' \end{array}\right. + 4\mathbf{S}O_2Ho_2 = \left.\begin{array}{l} \mathbf{S}O_2(N^vH_4O) \\ \mathbf{S}O_2\text{———} \\ \mathbf{S}O_2\text{———} \\ \mathbf{S}O_2(N^vH_4O) \end{array}\right\}('Cr'''_2O_6)^{vi}.$$

General Properties and Reactions of the Compounds of Chromium.—a. *Chromous compounds.*—These are of subordinate importance. They are distinguished by their powerful reducing properties. They rapidly absorb oxygen from the air, and are thus converted into chromic compounds.

b. *Chromic salts.*—These are derived from chromic oxide. Their solutions are violet-colored or green; they have a sweetish astringent

taste, an acid reaction towards litmus, and are poisonous. *Ammonia* produces a bulky precipitate of chromic hydrate, which is slightly soluble in a large excess of ammonia, yielding a peach-colored solution. *Caustic alkalies* precipitate green chromic hydrate, soluble in an excess of an alkali in the cold, but precipitated on boiling. *Sulphuretted hydrogen* gives no precipitate; *ammonic sulphide* precipitates chromic hydrate with evolution of sulphuretted hydrogen. When a chromium compound is fused with a mixture of sodic carbonate and nitre, an alkaline chromate is formed which dissolves in water, yielding a yellow solution.

c. *Chromates.*—The soluble chromates yield with *lead salts* a yellow precipitate of plumbic chromate; with *argentic nitrate*, red argentic chromate. When heated with concentrated *hydrochloric acid* they evolve chlorine, and the color of the liquid changes to green. *Sulphuretted hydrogen* reduces the chromates in acid solution to chromic salts with separation of sulphur; *alcohol* and *sulphurous acid* effect the same reduction.

Chromium compounds yield, with borax and with microcosmic salt, beads which are emerald-green, both in the oxidizing and in the reducing flame. Chromium compounds do not color flame, but yield a characteristic spark-spectrum containing bright lines in the green and in the blue.

MANGANESE, Mn.

Atomic weight = 55. *Molecular weight unknown. Sp. gr.* 7.99. *Atomicity* $''$, ^{iv}, ^{vi}, *and possibly* ^{viii}; *also a pseudo-triad and a pseudo-heptad. Evidence of atomicity:*

Manganous chloride, ...	$Mn''Cl_2$.
Manganic peroxide, ...	$Mn^{iv}O_2$.
Potassic manganate, ...	$Mn^{vi}O_2Ko_2$.
Potassic permanganate, ...	$\left\{\begin{matrix} Mn^{vii}O_3Ko \\ Mn^{vii}O_3Ko \end{matrix}\right.$

History.—The black oxide of manganese was known to the ancients, who were acquainted with its use in removing impurities from glass. They confounded it, however, with magnetic oxide of iron.

Occurrence.—Manganese is widely distributed in nature. It is never found native. The chief ores of manganese are the oxides, and of these the most important is manganic peroxide or *pyrolusite*, MnO_2. Others are dimanganic trioxide or *braunite*, Mn_2O_3; manganous dimanganic tetroxide or *haussmannite*, $\left\{\begin{matrix} MnO \\ MnO \end{matrix}\right. Mno''$. It also occurs as manganous sulphide in *manganese blende*, MnS'', and as manganous carbonate, $COMno''$, in *manganese spar*. It is present in small quantity in a number of other minerals, particularly silicates, so that in almost all rocks and soils traces of manganese are to be found. It occurs in minute quantities in the bodies of plants and animals.

Preparation.—Manganese cannot be reduced from its oxides by means of hydrogen; but the reduction may be effected by heating the oxide with carbon to intense whiteness. A mixture of 10 parts of

manganous dimanganic tetroxide, Mn_2O_2Mno'' (obtained by the ignition of the native peroxide), with 1 part of charcoal and 1 part of anhydrous borax, is heated to whiteness in a carbon crucible. The regulus of manganese thus obtained contains carbon, together with silicon derived from the ash of the charcoal. Pure manganese may be obtained by heating manganous manganic oxide (prepared from the artificial dioxide) in a lime crucible with a quantity of carbonized sugar insufficient for its total reduction. The lime crucible is placed inside a Hessian crucible, the intervening space is filled with charcoal, and the whole is heated in a wind-furnace.

Properties.—Manganese is a grayish-white metal with a reddish tinge. It is very hard and brittle. It fuses at a white heat. It oxidizes rapidly in moist air, and must therefore be preserved under rock-oil. Manganese is rapidly dissolved by dilute acids, and the finely divided metal decomposes water with evolution of hydrogen when gently warmed with it.

COMPOUNDS OF MANGANESE WITH THE HALOGENS.

MANGANOUS CHLORIDE, $MnCl_2$.—The anhydrous chloride is formed when the metal is burnt in chlorine, or when any of the oxides or the carbonate is heated in a current of dry hydrochloric acid. The residues from the preparation of chlorine by the action of hydrochloric acid upon manganic peroxide may be employed as a source of manganous chloride. This solution contains manganous chloride contaminated with ferric chloride, and sometimes with the chlorides of copper, barium, and calcium, together with an excess of hydrochloric acid. The solution is evaporated to expel the acid, diluted, and about an eighth of the solution precipitated with sodic carbonate. The precipitate, consisting of manganous carbonate and ferric hydrate, is well washed, added to the rest of the solution, and boiled with it. In this way the iron is precipitated by the manganous carbonate, whilst an equivalent quantity of manganese goes into solution as chloride:

$$\underset{\text{Ferric chloride.}}{'Fe_2Cl_6} + \underset{\text{Manganous carbonate.}}{3COMno''} + \underset{\text{Water.}}{3OH_2} = \underset{\text{Ferric hydrate.}}{'Fe_2Ho_6} + \underset{\text{Manganous chloride.}}{3MnCl_2} + \underset{\text{Carbonic anhydride.}}{3CO_2}.$$

The complete precipitation of the iron is ascertained by filtering a sample of the liquid and testing with potassic ferrocyanide. Should copper be present it is best removed with sulphuretted hydrogen. Calcium and barium are got rid of by precipitating the manganese with ammonic sulphide, washing the precipitate, and redissolving in hydrochloric acid. The concentrated solution deposits pink-colored monoclinic tabular crystals of the aquate, $MnCl_2,4OH_2$, which on heating are decomposed with evolution of hydrochloric acid. If, however, a solution of this compound be mixed with ammonic chloride, pink regular crystals of the double chloride, $MnCl_2,2NH_4Cl,OH_2$, are deposited, from

which, by careful heating, the water of crystallization may be expelled without further decomposition of the salt; and the anhydrous double chloride, when heated to a higher temperature, parts with ammonic chloride, leaving anhydrous manganous chloride. The anhydrous chloride forms a pink, micaceous, easily fusible mass, which is gradually decomposed by exposure to moist air.

The other chlorides of manganese—*manganic perchloride*, **Mn**Cl_4, and *dimanganic hexachloride*, $'$**Mn**$_2Cl_6$—are known only in solution. When the corresponding oxides—manganic peroxide, **Mn**O_2, and dimanganic trioxide, $'$**Mn**$_2O_3$—are dissolved in cold hydrochloric acid, these chlorides are formed; but on heating they are decomposed with evolution of chlorine, and the solutions contain manganous chloride.

Manganous bromide, **Mn**Br_2, is obtained like the chloride, which it closely resembles in properties. It also forms an aquate, **Mn**Br_2,4**O**H_2.

Manganous iodide, **Mn**I_2, is a white deliquescent mass.

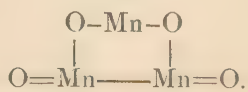
Manganous fluoride, **Mn**F_2, is obtained by dissolving manganous carbonate in hydrofluoric acid. It forms pale-red crystals, insoluble in pure water, soluble in aqueous hydrofluoric acid.

Manganic perfluoride, **Mn**F_4, is known only in solution. It is formed when manganic peroxide is dissolved in concentrated hydrofluoric acid. Water precipitates from the solution manganic peroxide, but on the addition of potassic fluoride a rose-red precipitate of the double fluoride, **Mn**F_4,2KF, is formed.

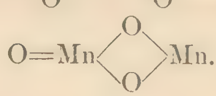
COMPOUNDS OF MANGANESE WITH OXYGEN.

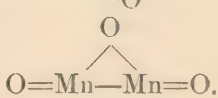
Manganese forms a large number of oxides, some of which are of great complexity. The following are the most important and best characterized:

Manganous oxide, . . . **Mn**O.

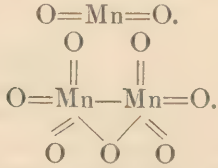
Manganous dimanganic tetroxide, ... $\left\{\begin{matrix}\textbf{Mn}O \\ \textbf{Mn}O\end{matrix}\right.Mno''$. 

or **Mn**Mno$''_2$. 

Dimanganic trioxide, . . **Mn**OMno$''$. 

or $\left\{\begin{matrix}\textbf{Mn}O \\ \textbf{Mn}O\end{matrix}\right.$O. 

Manganic peroxide, . . **Mn**O_2. O=Mn=O.

Permanganic anhydride, . $\left\{\begin{matrix}\textbf{Mn}O_3 \\ \textbf{Mn}O_3\end{matrix}\right.$O. 

Manganous oxide, **Mn**O, is formed when the carbonate or any of the higher oxides is heated in a current of hydrogen. It may be prepared by fusing anhydrous manganous chloride with sodic carbonate to which a little ammonic chloride has been added. It is a grayish-green powder, which, if it has been prepared at a low temperature, ab-

sorbs oxygen from the air and turns brown, but if it has been more strongly heated is permanent in air at ordinary temperatures. When heated to whiteness with exclusion of air, it fuses without loss of oxygen; if air be admitted, it is converted on heating into manganous dimanganic tetroxide. It cannot be reduced to metal by heating in a current of hydrogen. By heating in a current of hydrogen containing a trace of hydrochloric acid, it is obtained in the form of small green transparent octahedra with an adamantine lustre. Manganous oxide is the chief salifiable oxide of manganese.

MANGANESE HYDRATE, $\mathbf{Mn}Ho_2$, is obtained as a white precipitate when a caustic alkali is added to the solution of a manganous salt from which the air has been previously expelled by boiling. When exposed to the air it speedily turns brown from oxidation. It dissolves in solutions of ammonia salts.

MANGANOUS DIMANGANIC TETROXIDE (*Dimanganous manganite*) $'\mathbf{Mn}_2O_2Mno''$, or $\mathbf{Mn}Mno''_2$, occurs as *hausmannite* in brownish-black acute quadratic pyramids. This compound represents the most stable stage of oxidation of manganese: thus when the higher oxides are intensely heated, they evolve oxygen and are reduced to this stage, whilst, on the other hand, when manganous oxide or manganous carbonate is heated in air, oxygen is absorbed and the same compound is produced. The artificial oxide is a reddish-brown powder which, by gentle heating in a slow current of hydrochloric acid, is converted into crystals identical with those of the natural compound. Warm aqueous hydrochloric acid dissolves it with evolution of chlorine and formation of manganous chloride:

$$\underset{\text{Dimanganous manganite.}}{\mathbf{Mn}Mno''_2} + \underset{\text{Hydrochloric acid.}}{8HCl} = \underset{\text{Manganous chloride.}}{3\mathbf{Mn}Cl_2} + Cl_2 + \underset{\text{Water.}}{4\mathbf{O}H_2}.$$

Dilute oxy-acids—sulphuric or nitric—dissolve two-thirds of the manganese to form a manganous salt, whilst one-third remains as manganic peroxide:

$$\underset{\text{Dimanganous manganite.}}{\mathbf{Mn}Mno''_2} + \underset{\text{Nitric acid.}}{4\mathbf{NO}_2Ho} = \underset{\text{Manganous nitrate.}}{2\mathbf{N}_2O_4Mno''} + \underset{\text{Manganic peroxide.}}{\mathbf{Mn}O_2} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

There are no salts corresponding to this oxide. Its reactions are most readily accounted for on the assumption that it is a dimanganous manganite, as formulated in the two foregoing equations.

DIMANGANIC TRIOXIDE, $\mathbf{Mn}OMno''$ (or $'\mathbf{Mn}_2O_3$).—This compound occurs as the mineral *braunite* in brownish-black lustrous quadratic pyramids. It may be obtained as a black powder by heating any of the other oxides of manganese in oxygen.—A *dimanganic dioxydihydrate*, $\mathbf{Mn}Ho_2Mno''$ (or $'\mathbf{Mn}_2O_2Ho_2$), occurs as *manganite* in dark-gray rhombic crystals. The same compound is formed by the spontaneous oxidation of moist manganous hydrate in air.

The constitution of the above oxide and hydrate cannot be fixed with certainty. On the one hand, they both yield, with hot nitric acid, manganous nitrate with separation of manganic peroxide:

$$\underset{\text{Dimanganic trioxide.}}{\mathbf{Mn}_2O_3} + \underset{\text{Nitric acid.}}{2\mathbf{N}O_2Ho} = \underset{\text{Manganous nitrate.}}{\mathbf{N}_2O_4Mno''} + \underset{\text{Manganic peroxide.}}{\mathbf{Mn}O_2} + \underset{\text{Water.}}{OH_2}.$$

This reaction would be best accounted for by the first of the alternative formulæ above given, in which one atom of manganese is in the dyadic, the other in the tetradic condition. On the other hand, dimanganic trioxide occasionally acts as a basic oxide—in the formation of dimanganic hexachloride, for example—yielding salts in which the manganese is apparently a pseudo-triad. This behavior would be better explained by the formula $'\mathbf{Mn}_2O_3$.

MANGANIC PEROXIDE (*Manganic dioxide, black oxide of manganese*), $\mathbf{Mn}O_2$.—This is, as regards its usefulness, by far the most important of the ores of manganese. It occurs in large quantities as *pyrolusite*—sometimes in black or dark-gray rhombic prisms, more generally in fibrous or amorphous masses. It may be obtained artificially by carefully igniting manganous nitrate:

$$\underset{\text{Manganous nitrate.}}{\mathbf{N}_2O_4Mno''} = \underset{\text{Manganic peroxide.}}{\mathbf{Mn}O_2} + \underset{\text{Nitric peroxide.}}{'\mathbf{N}_2O_4}.$$

The ignited mass is extracted with boiling nitric acid, and the undissolved residue of manganic peroxide well washed and then moderately heated. It is also formed by the action of nitric acid upon manganous dimanganic tetroxide or dimanganic trioxide (p. 643). The same oxide is obtained in a hydrated state when a manganous salt is precipitated with an alkaline solution of a hypochlorite. When heated to low redness, manganic peroxide parts with one quarter of its oxygen, yielding dimanganic trioxide; at bright redness it parts with one-third of its oxygen, and is converted into manganous dimanganic tetroxide. It dissolves in cold hydrochloric acid with formation of manganic perchloride; on heating, chlorine is evolved and manganous chloride remains in solution. Nitric acid and dilute sulphuric acid are without action upon it; concentrated sulphuric acid dissolves it on heating with evolution of oxygen and formation of manganous sulphate. In presence of oxalic acid and other oxidizable substances it dissolves in dilute acids in the cold.—Manganic peroxide forms, with basic oxides, compounds which may be regarded as salts of a *manganous acid* of the formula $\mathbf{Mn}_5O_9Ho_2$. *Dipotassic pentamanganite*, $\mathbf{Mn}_5O_9Ko_2$, is a yellow powder which separates out when carbonic anhydride is passed into a solution of potassic manganate:

$$\underset{\text{Potassic manganate.}}{15\mathbf{Mn}O_2Ko_2} + \underset{\text{Carbonic anhydride.}}{18\mathbf{C}O_2} + \underset{\text{Water.}}{9OH_2} = \underset{\text{Dipotassic pentamanganite.}}{\mathbf{Mn}_5O_9Ko_2} +$$

$$\underset{\text{Potassic permanganate.}}{5'\mathbf{Mn}_2O_6Ko_2} + \underset{\text{Hydric potassic carbonate.}}{18\mathbf{C}OHoKo}.$$

Manganic peroxide is used in the production of colorless glass (p. 481). It also serves as a cheap source of oxygen, when this gas is required in

large quantities; but its chief employment is in the preparation of chlorine for the manufacture of bleaching-powder.

Regeneration of Manganic Peroxide. Weldon's Process.—Formerly the residues of manganous chloride obtained in the manufacture of chlorine were allowed to run to waste. At the present day, by means of a process devised by Weldon, the greater part of the manganese is reconverted into manganic peroxide and recovered in this form. For this purpose the chlorine residues (see Preparation of Chlorine, p. 151), which contain, along with manganous chloride, ferric chloride and other impurities, are first treated with calcic carbonate in order to neutralize the excess of acid and to precipitate the iron. To the clear solution of manganous chloride and calcic chloride thus obtained milk of lime is added in the proportion of $1\frac{1}{2}$ molecules of calcic hydrate to each molecule of manganous chloride. The mixture of manganous hydrate, calcic hydrate and calcic chloride is then heated by means of a current of steam to a temperature of from 55° to 75° C. (131°–167° F.), after which air is blown through the liquid. Manganous hydrate alone is oxidized only to hydrated dimanganic trioxide, but in presence of excess of lime a rapid oxidation of the manganous hydrate to manganic peroxide occurs. The manganic peroxide is obtained in combination with calcic oxide, as calcic manganite, $\mathbf{Mn}OCao''$, and it is upon the formation of this compound that the greater readiness of oxidation depends. The oxidation is continued until about three-fourths of the manganese has been converted into peroxide. About 2 cubic metres of air are blown in for every pound of manganic peroxide regenerated, and the time required for the regeneration of a ton of the peroxide is five hours. The "manganese-mud" is allowed to settle and, after running off the liquid, is pressed into a solid cake. In this form it is employed in the preparation of chlorine. It usually contains about 33 per cent. of manganic peroxide in combination with lime.

Permanganic anhydride, $\left\{\begin{matrix}\mathbf{Mn}O_3\\ \mathbf{Mn}O_3\end{matrix}\right.O$.—This compound is obtained by the action of sulphuric acid upon potassic permanganate. The finely powdered *pure* salt (the absence of chlorine is especially essential, as, otherwise, dangerous explosions may occur, owing to the formation of oxides of chlorine) is gradually added to well-cooled concentrated sulphuric acid. From the olive-green solution thus obtained reddish-brown oily drops of the anhydride gradually separate—the more readily if the solution be allowed to absorb moisture from the air—and sink to the bottom. Permanganic anhydride is a very unstable compound: when rapidly heated it decomposes with a violent explosion. It undergoes slow decomposition at ordinary temperatures, evolving bubbles of oxygen which carry with them violet fumes of the anhydride. It is a powerful oxidizing agent: when brought in contact with paper, alcohol, or other organic substances, it causes their ignition. It rapidly absorbs moisture from the air, and dissolves in water with great rise of temperature, yielding a violet-colored solution of permanganic acid, a portion of the substance being at the same time decomposed by the heat evolved. The acid cannot be isolated.

OXY-SALTS OF MANGANESE.

a. Manganous Salts.

Manganous nitrate, $N_2O_4Mno'',6OH_2$, is prepared by dissolving the carbonate in nitric acid. It is difficultly crystallizable and very deliquescent. When heated it fuses, and is converted into manganic peroxide.

Manganous carbonate, $COMno''$, occurs native as *manganese spar* in pink hexagonal crystals. The native compound generally contains iron, calcium, and magnesium. It is precipitated as a white powder when an alkaline carbonate is added to the solution of a manganous salt. When exposed to the air in a moist state it speedily becomes brown from oxidation.

MANGANOUS SULPHATE, SO_2Mno''.—Commercial black oxide of manganese is made into a paste with concentrated sulphuric acid, and the mixture is heated in a crucible, first gently, and afterwards to redness, in order to convert the ferric sulphate into insoluble ferric oxide. The mass is lixiviated, and the solution is digested with a small quantity of manganous carbonate, in order to precipitate the last traces of iron. At a temperature below 6° C. pink rhombic crystals of the formula $SOHo_2Mno'',6OH_2$, isomorphous with ferrous sulphate, are deposited. From 7° to 20° C. triclinic crystals of the formula $SOHo_2Mno'',4OH_2$, isomorphous with cupric sulphate, are obtained. Several other aquates are known. All these salts become anhydrous at 200° C. (392° F.).—With the sulphates of the alkalies manganous sulphate forms double salts, isomorphous with the corresponding double sulphates of the other metals of the dyadic group with the alkalies. *Dipotassic manganous sulphate*, $\left\{\begin{array}{l} SO_2Ko \\ Mno'',6OH_2 \\ SO_2Ko \end{array}\right.$ forms monoclinic crystals.

Aluminic manganous tetrasulphate, $$\left\{\begin{array}{l} SO_2— \\ SO_2— \\ Mno''('Al'''_2O_6)^{vi},24OH_2 \\ SO_2— \\ SO_2— \end{array}\right.$$ — This double sulphate occurs as the mineral *apjohnite*. It has the composition of an alum, and is frequently termed *manganese aluminium alum*, but inasmuch as it possesses, in common with the other salts in which two atoms of a monad metal in alum are displaced by one atom of a dyad metal, a crystalline form differing from that of the ordinary alums, many chemists refer it to a separate class—that of the *pseudo-alums*. Other pseudo-alums are known containing iron, zinc, and magnesium, as dyad metals.

Manganous dithionate, $\left\{\begin{array}{l} SO_2 \\ SO_2 \end{array}\right. Mno''3OH_2$. — Finely powdered manganic peroxide is suspended in water, and sulphurous anhydride is passed into the liquid, avoiding any rise of temperature. The salt crystallizes in pale-red soluble rhombohedra. It forms the starting-point for the preparation of the other dithionates.

Manganous silicate, $SiOMno''$, occurs native as *rhodonite* in brownish-red crystals.—*Dimanganous silicate*, $SiMno''_2$, forms the mineral *tephroite*, which crystallizes in quadratic forms.

b. Manganic Salts.

Manganic sulphate (*Dimanganic trisulphate*) $\left.\begin{array}{l}SO_3-\\SO_3-\\SO_3-\end{array}\right]('Mn'''_2O_6)^{vi}$, is obtained by the action of sulphuric acid upon hydrated manganic peroxide. It is a green powder which deliquesces on exposure to air, and is decomposed at 160° C. (320° F.) with evolution of oxygen.

Dipotassic dimanganic tetrasulphate (*Manganese alum*),

$$\left.\begin{array}{l}SO_2Ko-\\SO_2-\\SO_2-\\SO_2Ko-\end{array}\right]('Mn'''_2O_6)^{vi},24OH_2,$$

is formed when potassic sulphate is added to a solution of manganic sulphate in dilute sulphuric acid. It crystallizes from very concentrated solutions in violet-colored regular octahedra. Excess of water decomposes it, manganic hydrate being deposited. With ammonic sulphate a corresponding *ammonia manganese alum* is obtained.

THE MANGANATES.

Neither manganic anhydride, MnO_3, nor manganic acid, MnO_2Ho_2, have been prepared; but salts of this acid, called *manganates*, are known. These are isomorphous with the corresponding sulphates.

Potassic manganate, MnO_2Ko_2.—When manganic peroxide is fused with caustic potash a deep-green mass is obtained, which contains potassic manganate. When the fusion is performed out of contact with air, the reaction takes place according to the equation—

$$\underset{\text{Manganic peroxide.}}{3MO_2} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic manganate.}}{MnO_2Ko_2} + \underset{\text{Dimanganic trioxide.}}{'Mn_2O_3} + \underset{\text{Water.}}{OH_2};$$

but if air be admitted, or if nitre or potassic chlorate be added to the mixture, the whole of the manganic peroxide is converted into manganate. The mass dissolves without decomposition in a small quantity of water, and the dark-green solution deposits, on evaporation *in vacuo*, rhombic crystals of potassic manganate, which, when first prepared, are almost black, and display metallic lustre, but become dull and green-colored by exposure to the air. Potassic manganate is stable only in solutions which contain an excess of free caustic alkali; when these solutions are diluted with a large quantity of water, the manganate is decomposed with separation of manganic peroxide and formation of potassic permanganate:

$$\underset{\text{Potassic manganate.}}{3MnO_2Ko_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Potassic permanganate.}}{\left\{\begin{array}{l}MnO_3Ko\\MnO_3Ko\end{array}\right.} + \underset{\text{Manganic peroxide.}}{MnO_2} + \underset{\text{Potassic hydrate.}}{4KHo.}$$

The color of the solution changes at the same time from green to violet. The same decomposition occurs when carbonic anhydride is passed into the alkaline solution of a manganate.

Sodic manganate, $\mathbf{Mn}O_2Nao_2$, is prepared in a similar manner by fusing manganic peroxide with sodic nitrate. It is deposited from its alkaline solutions in crystals of the formula $\mathbf{Mn}O_2Nao_2.10\mathbf{O}H_2$, isomorphous with Glauber's salt.

Baric manganate, $\mathbf{Mn}O_2Bao''$, is obtained by fusing manganic peroxide with baric nitrate and extracting the mass with water. It is a green powder, insoluble in water. Acids decompose it.

PERMANGANIC ACID AND THE PERMANGANATES.

Permanganic acid, $\left\{\begin{matrix}\mathbf{Mn}O_3Ho \\ \mathbf{Mn}O_3Ho\end{matrix}\right.$, is know only in solution. The solution is obtained, as already described (p. 645), by dissolving permanganic anhydride in water, or, more readily, by decomposing a solution of baric permanganate with the equivalent quantity of sulphuric acid. The solution is deep-red by transmitted and blue by reflected light. When heated, or even when exposed to light, it evolves oxygen with separation of hydrated manganic peroxide.

POTASSIC PERMANGANATE, $\left\{\begin{matrix}\mathbf{Mn}O_3Ko \\ \mathbf{Mn}O_3Ko\end{matrix}\right.$.—The green mass obtained in the preparation of potassic manganate (p. 647) is extracted with boiling water. In this way the manganate is decomposed with formation of permanganate (p. 647). If an excess of alkali is present carbonic anhydride ought to be passed into the liquid. The precipitate of hydrated manganic peroxide is removed by filtration through asbestos or glass-wool (filters of paper, calico, or other organic substance would be attacked). The clear liquid, when allowed to evaporate, deposits crystals of potassic permanganate. These are isomorphous with potassic perchlorate. For this reason, if potassic chlorate has been employed in the preparation of the permanganate, the latter salt is apt to be contaminated with perchlorate, from which it cannot be freed by crystallization, as the two salts crystallize together in all proportions. Potassic permanganate forms large rhombic prisms, which are deep-red by transmitted and almost black by reflected light, with a metallic lustre. The salt is soluble in 16 parts of water at ordinary temperatures, more readily soluble in boiling water, yielding a solution of a deep purple color. The solution is a powerful oxidizing agent and destroys most organic substances. A solution of crude potassic permanganate, or more commonly of the sodium salt, is employed as a disinfectant under the name of "Condy's Disinfecting Fluid." By exposure to the air the solution of permanganate is gradually reduced by organic matter from the atmosphere, changing its color from purple to blue, and at last to green. Owing to these changes this substance was formerly known as *mineral chameleon*. Boiling with concentrated caustic alkali converts potassic permanganate into manganate with evolution of oxygen:

$$\underset{\text{Potassic permanganate.}}{\left\{\begin{matrix}\mathbf{Mn}O_3Ko \\ \mathbf{Mn}O_3Ko\end{matrix}\right.} + \underset{\text{Potassic hydrate.}}{2KHo} = \underset{\text{Potassic manganate.}}{2\mathbf{Mn}O_2Ko_2} + O + \underset{\text{Water.}}{\mathbf{O}H_2}.$$

the chemical change being accompanied by a change in the color of the liquid from purple to green. When the dry salt is heated to 240° C. (464° F.) it evolves oxygen and is converted into a mixture of manganate and manganic peroxide:

$$\left\{\begin{matrix} \mathbf{Mn}O_3Ko \\ \mathbf{Mn}O_3Ko \end{matrix}\right. = \mathbf{Mn}O_2Ko_2 + \mathbf{Mn}O_2 + O_2.$$

Potassic permanganate. Potassic manganate. Manganic peroxide.

Sodic permanganate, $\left\{\begin{matrix} \mathbf{Mn}O_3Nao \\ \mathbf{Mn}O_3Nao \end{matrix}\right.$, is prepared like the potassium salt. It is manufactured on a large scale as a disinfectant by fusing black oxide of manganese with crude caustic soda in shallow iron vessels.

Ammonic permanganate, $\left\{\begin{matrix} \mathbf{Mn}O_3Amo \\ \mathbf{Mn}O_3Amo \end{matrix}\right.$, is obtained by decomposing the barium salt with ammonic sulphate. It is isomorphous with the potassium salt, which it closely resembles, but is more soluble. It is readily decomposed on heating.

Baric permanganate, $\left\{\begin{matrix} \mathbf{Mn}O_3 \\ \mathbf{Mn}O_3 \end{matrix}\right.Bao''$.—Carbonic anhydride is passed through water in which baric manganate is suspended, and, after filtering from the baric carbonate, the red solution thus obtained is rapidly evaporated. It forms large deep-red rhombic crystals, readily soluble in water.

Argentic permanganate, $\left\{\begin{matrix} \mathbf{Mn}O_3Ago \\ \mathbf{Mn}O_3Ago \end{matrix}\right.$, separates in large red crystals, when warm solutions of argentic nitrate and potassic permanganate are mixed and allowed to stand. It is sparingly soluble in cold water.

COMPOUND OF MANGANESE WITH OXYGEN AND CHLORINE.

Permanganic hexoxy-dichloride, $\left\{\begin{matrix} \mathbf{Mn}O_3Cl \\ \mathbf{Mn}O_3Cl \end{matrix}\right.$—In order to obtain this compound sodic chloride is added to a solution of potassic permanganate in concentrated sulphuric acid. A yellow gas is evolved, which condenses in a freezing mixture, yielding a greenish-brown liquid. In contact with moist air it emits red fumes. Water decomposes it with formation of permanganic and hydrochloric acids; but these substances at once react upon each other, yielding chlorine and manganic peroxide. It explodes violently on heating.

COMPOUND OF MANGANESE WITH SULPHUR.

MANGANOUS SULPHIDE, $\mathbf{Mn}S''$, occurs native as *manganese blende* in steel-gray granular masses, and occasionally in black cubical crystals. The same compound is obtained as a greenish-gray powder by heating any of the oxides of manganese in a current of sulphuretted hydrogen. Alkaline sulphides produce in solutions of manganous salts a flesh-colored amorphous precipitate of hydrated manganous sulphide, which is readily soluble in dilute acids, even in acetic, with evolution of sulphuretted hydrogen, and when exposed to the air becomes brown from oxidation. By prolonged contact, or by heating, with an excess of the alkaline sulphide, the precipitate is transformed into a green crystalline powder of the formula $3\mathbf{Mn}S,\mathbf{O}H_2$.—Manganous sulphide unites with the sulphides of the alkali metals to form double

compounds. A double sulphide of this description is *disulphopotassic trimanganous disulphide*, $\begin{matrix}\mathbf{MnKs}\\\mathbf{MnKs}\end{matrix}\mathrm{Mns}''$.

Manganic disulphide, $\mathbf{Mn}S''_2$, occurs in nature as the mineral *hauerite* in dark reddish-brown regular crystals.

CHARACTERISTIC PROPERTIES AND REACTIONS OF THE COMPOUNDS OF MANGANESE.—The manganous salts are of a pale rose color. *Caustic alkalies* precipitate white manganous hydrate, which speedily oxidizes and becomes brown. *Ammonia* only partially precipitates the manganese as hydrate; in presence of an excess of ammonic chloride ammonia does not produce any precipitate, but the solution on standing absorbs oxygen from the air, and deposits hydrated trimanganic tetroxide. *Alkaline carbonates* precipitate basic manganous carbonate; *baric carbonate* does not precipitate manganous salts in the cold. *Ammonic sulphide* precipitates flesh-colored hydrated manganous sulphide, soluble in dilute acids, even in acetic acid.

All manganous compounds, when fused with sodic carbonate and nitre, yield a green mass containing an alkaline manganate. With borax or microcosmic salt, they give a bead which is amethyst-colored in the oxidizing flame, and colorless in the reducing flame. Manganous chloride colors the non-luminous flame green: the spectrum of the flame exhibits lines in the green and yellow. The spark-spectrum of manganese contains a large number of lines.

IRON, Fe.

Atomic weight = 56. *Molecular weight unknown.* *Sp. gr.* 7.8. *Atomicity*'', ^{iv}, *and* ^{vi}. *Evidence of atomicity:*

Ferrous chloride, ...	$\mathbf{Fe}''Cl_2$.
Ferric disulphide, ...	$\mathbf{Fe}^{iv}S''_2$.
Ferric chloride, ...	$'\mathbf{Fe}'''_2,Cl_6$.
Potassic ferrate, ...	$\mathbf{Fe}^{vi}O_2Ko_2$.

History.—The process of obtaining iron from its ores has been known from very early times. Owing to its abundance, to the ease with which it can be reduced to the metallic state, and to its valuable properties, it is by far the most important of the metals.

Occurrence.—Iron is the most abundant and widely diffused of the metals, with the exception of aluminium. Native iron, which is of rare occurrence, may be divided into two kinds—*meteoric iron*, of extraterrestrial origin, and *telluric iron*. Meteoric iron sometimes occurs in considerable masses: the largest have been found on the island of Disko, off the coast of Greenland, where there are fifteen of these blocks, the two largest weighing 21,000 and 8,000 kilos. Weapons and implements of meteoric iron have been found among the Eskimos, and also among tribes in Central Africa. Meteoric iron is never pure: it contains varying quantities of other metals, notably nickel and cobalt, the proportion of the first of these sometimes ranging as high as 30 per cent. On the snow-fields of Northern Europe and Asia the snow is

found to inclose minute magnetic particles possessing the composition of meteoric iron. It is probable that this meteoric dust is continually falling upon the earth; but its presence can be detected with certainty only in localities which, like the above, are sufficiently remote from all sources of terrestrial dust. Telluric iron occurs in small spiculæ disseminated through various basalts and lavas. Masses of terrestrial iron have also been observed in cases in which the fire of burning coal-mines has acted upon ores of iron. This variety is known as *natural steel.*

Iron most frequently occurs in combination with oxygen or sulphur. In combination with oxygen it is found as ferric oxide, $'Fe_2O_3$, in *red hœmatite,* or *specular iron ore;* as *ferrous diferric tetroxide,* $\left\{\begin{matrix}FeO\\FeO\end{matrix}\right.Feo''$, in *magnetic iron ore;* as tetraferric trioxyhexahydrate, $Fe_4O_3Ho_6$, in *brown hœmatite;* and as ferrous carbonate, $COFeo''$ in *spathose iron ore.* The disulphide, FeS''_2, is of very common occurrence as *iron pyrites.* Iron is also found in the form of a sulphide in *copper pyrites,* $\left\{\begin{matrix}FeS\\FeS\end{matrix}\right.('Cu'_2S''_2)''$. Silicates of iron are contained in nearly all rocks, and by the disintegration and decomposition of these rocks the oxide of iron is produced which imparts to the soil its red color. From the soil plants extract the iron which is a necessary constituent of the chlorophyll, or green coloring matter of their leaves. Iron is also a necessary constituent of the hæmoglobin, or red coloring matter of the blood. The chlorophyll of plants enables them, with the aid of sunlight, to decompose the carbonic anhydride and aqueous vapor of the atmosphere: a portion of the oxygen resulting from this decomposition is evolved, whilst the other products of decomposition are used in building up the tissues and principles of the plant. The hæmoglobin of the blood acts as a carrier of the oxygen which is absorbed during respiration, and which serves for the oxidation of the animal tissues. In this way the respiratory functions both of plants and of animals are dependent upon the presence of iron.

The presence of iron in extra-terrestrial space is proved by its occurrence in meteorites, and, further, by the results of spectrum analysis, which show that this metal is present in the sun and in many of the fixed stars.

Extraction.—The important and complex subject of the metallurgy of iron can only be briefly sketched here.

The compounds of iron from which the metal is extracted are the oxides, the hydrates, and the carbonate. The chief ores are: *magnetic iron ore, red hœmatite, brown hœmatite, spathose iron ore,* and *clay iron-stone* or *argillaceous iron ore,* which is a spathose iron mixed with clay or sand. *Black band* is a variety of clay iron-stone containing from 20 to 25 per cent. of coal. The ores are first *calcined* or roasted. In this process water and carbonic anhydride are expelled, whilst most of the sulphur, which may be present, is oxidized and burnt off as sulphurous anhydride. At the same time the ore is rendered more friable and porous. The ore is then reduced by heating with coal, limestone, and occasionally silicates, in a hot-blast furnace. This furnace consists of a lofty shaft of strong masonry lined with fire-brick. The internal

space is narrower towards the bottom, where the molten metal collects. The furnace is first lighted or *blown in*, after which alternate layers of a mixture of calcined ore and limestone on the one hand, and of coal on the other, are thrown in at the top until the furnace is full. A powerful blast of air, previously heated to from 350° to 700° C. (662–1292° F.), is forced in through pipes or *tuyères* placed at the bottom of the furnace. The chemical changes which occur in the furnace are as follows: The oxygen of the air on entering the furnace unites with the carbon to form carbonic anhydride, which in turn is converted into carbonic oxide by contact with the heated carbon. The carbonic oxide in passing upwards over the heated ferric oxide reduces it to finely-divided iron. The part of the furnace in which this change occurs is termed the "zone of reduction." At the same time the fusible flux of silicate of lime coats the particles of metal and protects them from oxidation. As the reduced iron sinks into the hotter parts of the furnace it begins to combine with carbon; this part of the furnace is therefore known as the "zone of carburation." At this point the iron also takes up phosphorus derived by reduction from phosphates contained in the ore. The metal gradually sinks till it reaches the hottest part of the furnace—the "zone of fusion"—when it melts and runs down to the *hearth* or lowest part of the furnace. Here it would be exposed to the danger of oxidation from the blast; but the fusible slag floats on the surface of the molten metal and protects it. The excess of slag runs off regularly through an opening. From time to time the molten iron is tapped and cast into bars known as *pigs*. As fast as the charge in the furnace sinks, fresh charges of ore, limestone, and coal are introduced. In this way a blast-furnace may be kept continuously at work for many years.

The crude iron thus obtained, known as *pig iron* or *cast iron*, contains from 3 to 6 per cent. of carbon, together with varying quantities of manganese, silicon, sulphur, phosphorus, arsenic, and antimony. The carbon is present in two forms: partly in chemical combination, and partly as particles of graphite mechanically disseminated throughout the mass of the metal. When cast iron is dissolved in acids, the carbon displays a different behavior according to the form in which it is present: the mechanically disseminated carbon is left behind unchanged, whilst the chemically combined carbon enters into combination with hydrogen to form complex hydrocarbons, gaseous and liquid. According to color and other properties, the following varieties of cast iron are distinguished: *White cast iron*, which contains the whole of its carbon in the combined condition; and *gray cast iron*, which, in addition to the combined carbon, contains graphite disseminated throughout its mass. Various intermediate stages are classed as *mottled cast irons*. *Spiegeleisen*, *spiegel*, or *specular pig iron* is a white iron containing the highest percentage (3.5 to 6 per cent.) of combined carbon. White iron is formed when the temperature of the blast furnace is low. It contracts on solidification, and therefore cannot be used for castings. Gray iron is formed when the temperature is high. It expands on solidifying, and is suitable for foundry work.

Cast iron is brittle and cannot, as a rule, be forged. In order to

impart to it the property of malleability, the greater portion of the carbon and the other foreign substances must be removed by a process of oxidation. In this way the cast iron is converted into *wrought iron.* The process most commonly employed in the production of wrought iron is that of *puddling:* the wrought iron is fused along with powdered hæmatite on the hearth of a reverberatory furnace, employing a flux of blast-furnace slag. During the process, the metal is stirred to promote oxidation. The silicon is first converted into silicic anhydride, which is taken up by the bases of the slag; afterwards, the carbon is burnt off as carbonic anhydride. A comparatively low temperature is essential to the effectual removal of the phosphorus, since at a high temperature the iron reduces the phosphates contained in the slag and takes up phosphorus.

Wrought iron contains from 0.15 to 0.5 per cent. of carbon. The lower the proportion of carbon the more malleable and the less readily fusible is the iron. Rolled and hammered wrought iron, containing 0.3 per cent. of carbon, has a fibrous structure; if the percentage rises to 0.5, the structure becomes granular and crystalline. The hardness of the metal also increases with the percentage of carbon. Wrought iron is of a clear gray color, and capable of taking a high polish. At a red heat it softens and may be welded. The physical properties of iron are powerfully modified by the presence of minute quantities of various impurities: thus sulphur renders the metal "red-short"—that is, brittle at high temperatures; phosphorus renders it "cold-short," or brittle at ordinary temperatures.

If the proportion of chemically combined carbon in iron lies between 0.6 and 2 per cent., the product is known as *steel.* In chemical composition, steel therefore stands midway between wrought iron and cast iron, and it may in fact be produced from the former of these by increasing, and from the latter by diminishing, the proportion of carbon present. Steel was formerly exclusively prepared from wrought iron by the *cementation process.* In this process bars of wrought iron are packed in powdered charcoal or soot, and heated to bright redness for from seven to ten days, according to the nature of the product required. In this way the iron takes up the carbon necessary for its conversion into steel. The exact mode in which this is accomplished is not perfectly understood, though various hypotheses have been made with regard to this process. The bars of steel, after their conversion, exhibit a peculiar blistered appearance due to the production of gas within the mass of the metal. This imperfection is removed by hammering and rolling, or by melting the steel. *Puddled steel* is an inferior quality of steel prepared from cast iron by arresting the process of puddling at a point short of the production of wrought iron. In the *Bessemer process* of steel making, cast iron is melted, and then transferred to a vessel known as a *converter*, through the bottom of which a powerful blast of air is blown. The silicon, manganese, and carbon are thus oxidized, and so great is the heat evolved that the temperature of the molten metal rises considerably. Formerly the process was interrupted at the point of formation of steel, but at the present day the oxidation is carried on until the whole of the carbon is removed—a point much more readily

ascertained—after which the molten spiegel is added in quantity exactly sufficient to convert the whole into steel.

Steel is of a clear gray color, and possesses a granular structure. It may be forged and welded like wrought iron, and fuses at a lower temperature than the latter. It possesses the property of becoming intensely hard and brittle when heated to redness and then suddenly cooled—for example, by plunging into water. This hardness and brittleness can be removed in any required degree by heating the hardened steel to temperatures between 200° and 300° C. (392–572° F.) and then allowing it to cool. This process is known as *tempering*. The lower the temperature employed, the harder will be the resulting steel. If the surface of the object to be tempered be first polished, it will exhibit shades of color on heating, due to the formation of films of oxide of varying thickness. By observing these colors the workman is enabled to judge with sufficient accuracy of the temperature which he is employing. The specific gravity of hardened steel is somewhat lower than that of wrought steel. In hardened steel the whole of the carbon is present in the combined state, whereas wrought steel also contains graphitic carbon.

Preparation of Pure Iron.—The purest iron of commerce is pianoforte wire, which contains only about 0.3 per cent. of impurities—for the most part carbon. Chemically pure iron is prepared by heating the pure oxalate or oxide in a current of hydrogen. It is thus obtained in the form of a black powder, which, when the reduction has been effected at a sufficiently low temperature, is pyrophoric, spontaneously oxidizing with incandescence when exposed to the air. If heated to a higher temperature during reduction, the product is denser and no longer spontaneously oxidizable. It may be fused into a regulus in a lime crucible by means of the oxyhydrogen flame. Very pure iron may also be obtained by fusing wrought iron with ferric oxide under a layer of melted glass free from lead.

Properties.—Pure iron is almost silver-white, and is capable of taking a high polish. It has a specific gravity of 7.84. It is softer, more malleable, and less tenacious than wrought iron. It is fusible only at the very highest temperatures. It does not undergo any change in dry air at ordinary temperatures; but in moist air containing carbonic anhydride it becomes coated with ferric hydrate or iron rust. The process of rusting takes place very slowly at first, but goes on rapidly as soon as a thin coating of rust has been formed upon the surface of the metal. When heated in air, iron becomes coated with ferrous diferric tetroxide, $\left\{\begin{matrix}FeO\\FeO\end{matrix}\right.Feo''$, which, on hammering, flies off in scales (*smithy scales*). It burns brilliantly when heated in oxygen, emitting showers of dazzling sparks, and yielding the foregoing oxide. It burns also in sulphur vapor. It combines directly with the halogens, and at a high temperature with carbon. At a red heat it decomposes water, with evolution of hydrogen, and formation of ferrous diferric tetroxide. Dilute hydrochloric or sulphuric acid dissolves it with evolution of hydrogen, and when the metal contains chemically combined carbon, hydrocarbons are mixed with the hydrogen, imparting to it a peculiar and disa-

greeable odor. Nitric acid of sp. gr. 1.35, or lower, dissolves iron with violent evolution of nitrous fumes and formation of ferric nitrate; but under certain circumstances iron may be kept immersed for any length of time in nitric acid without the slightest action, or diminution of its brightness of surface. This condition, which is known as the *passive state* of iron, is produced when the metal is immersed in nitric acid of sp. gr. 1.45 or higher. The iron which has been thus rendered passive is not acted upon by dilute nitric acid. The same condition is induced when iron is made the positive plate of a voltaic couple in nitric acid: for example, when it is introduced into nitric acid of sp. gr. 1.35 in contact with a piece of platinum. The platinum may then be removed, and the iron remains passive. Passive iron does not precipitate copper from its solutions, but if a piece of passive iron which has been dipped into the solution of a copper salt be scratched, the copper is instantly deposited on the whole surface of the iron. Passive iron is powerfully electronegative towards ordinary iron, and a voltaic couple may be constructed consisting of passive iron in concentrated nitric acid and ordinary iron in a solution of sodic sulphate, the two liquids being separated by a porous diaphragm. The phenomenon of passivity in iron depends upon the formation of a thin film of ferrous diferric tetroxide upon the surface of the metal. Thus iron may be rendered passive by moderately heating it. The deposition of copper in the case above described depends upon the fact that by scratching the passive metal the film of oxide is removed at that part and a surface of iron exposed; a voltaic action then sets up between the electro-positive iron and the electro-negative oxide, and the hydrogen which is liberated on the surface of the latter reduces it, converting it into iron, which in its turn reduces the copper. The voltaic action between iron and ferrous diferric tetroxide may be employed in rendering the metal passive: thus if one end of a bright iron wire be heated so as to oxidize it, and then the wire be dipped, with the oxidized end first, into nitric acid of sp. gr. 1.35, the whole wire is rendered passive.—Iron is attracted by the magnet, and may also be magnetized, but parts with its magnetism almost instantaneously, whilst steel is capable of permanently assuming the polar state.

COMPOUNDS OF IRON WITH THE HALOGENS.

a. Ferrous Compounds.

FERROUS CHLORIDE, $\mathbf{Fe}Cl_2$, is prepared by heating iron in gaseous hydrochloric acid. A solution of this compound is obtained by dissolving iron in aqueous hydrochloric acid. The anhydrous chloride sublimes in colorless fusible six-sided scales. When volatilized in an atmosphere of gaseous hydrochloric acid, it possesses a vapor density lying between the densities required for the molecular formulæ $\mathbf{Fe}Cl_2$ and $''\mathbf{Fe}_2Cl_4$ respectively. It is therefore probable that the iron in this compound is at lower temperatures tetradic and at higher temperatures dyadic. When heated in air ferrous chloride is converted into ferric chloride, which volatilizes, and ferric oxide:

$$\begin{array}{ccccccccc} 6FeCl_2 & + & 3O & = & 'Fe_2Cl_6 & + & 'Fe_2O_3. \\ \text{Ferrous} & & & & \text{Ferric} & & \text{Ferric} \\ \text{chloride.} & & & & \text{chloride.} & & \text{oxide.} \end{array}$$

It is deliquescent, and soluble both in water and in alcohol. The aqueous solution, when concentrated out of contact with air, deposits pale-green deliquescent crystals of the formula $FeCl_2,4OH_2$. The crystals absorb oxygen from the air and undergo decomposition. Ferrous chloride forms double compounds with the chlorides of the alkalies. *Potassic ferrous chloride,* $FeCl_2,2KCl,2OH_2$, is deposited from mixed solutions of its component chlorides in bluish-green monoclinic crystals.

Ferrous bromide, $FeBr_2$, is obtained as a yellowish crystalline mass when bromine vapor is passed over iron filings heated to low redness. The aqueous solution, prepared by dissolving iron in hydrobromic acid, deposits on concentration the aquate, $FeBr_2,6OH_2$, in green tabular crystals.

Ferrous iodide, FeI_2, is obtained as a gray laminated mass by heating iron filings in a closed crucible and adding small quantities of iodine. An excess of iodine is then added, and the heating is continued until vapors of iodine cease to escape. The aqueous solution, which is readily obtained by digesting iron filings with iodine and water, deposits on evaporation green crystals of the formula $FeI_2,4OH_2$.

Ferrous fluoride, FeF_2.—When iron is dissolved in hydrofluoric acid, sparingly soluble green crystals of the compound $FeF_2,8OH_2$ are deposited, which, when heated with exclusion of air, become anhydrous.

b. *Ferric Compounds.*

FERRIC CHLORIDE, $'Fe_2Cl_6$. *Molecular volume* $\square\square$.—This compound is obtained in the anhydrous state by gently heating iron wire in a current of chlorine, and in solution by dissolving ferric oxide in hydrochloric acid or iron in aqua-regia. The anhydrous compound forms dark-brown hexagonal plates, which possess a green metallic lustre, and appear red by transmitted light. It is fusible, and volatilizes more readily than the ferrous compound. It deliquesces in moist air, and is readily soluble in water; the dilute solution is yellow, the concentrated solution is dark-brown, and of an oily consistency. It is also soluble in alcohol and in ether: the latter solvent extracts the compound from the aqueous solution when agitated with it. The aqueous solution when concentrated over sulphuric acid deposits yellow prismatic crystals of the compound $'Fe_2Cl_6,12OH_2$, and at a still higher degree of concentration brownish-red crystals having the formula $'Fe_2Cl_6,6OH_2$. When the hydrated chloride is heated, it parts with water and hydrochloric acid, yielding an oxychloride, which at a higher temperature decomposes into volatile anhydrous ferric chloride and ferric oxide. A dilute aqueous solution, containing less than 4 per cent. of ferric chloride, is decomposed on heating into soluble colloidal ferric hydrate (p. 658) and free hydrochloric acid, this chemical change being accompanied by a change in the color of the liquid from yellow to red. When a concentrated aqueous solution is evaporated by heat it parts with hydrochloric acid and an insoluble oxychloride of varying composition separates out. —Ferric chloride forms numerous double compounds. *Potassic ferric chloride,* $Fe_2Cl_6,4KCl,2OH_2$, is deposited in garnet-red crystals from mixed solutions of ferric and potassic chlorides. Anhydrous ferric chloride absorbs gaseous ammonia, yielding the compound $'Fe_2Cl_6,2NH_3$, which in appearance is indistinguishable from ferric chloride.

Ferric bromide, $'\mathbf{Fe}_2Br_6$, is prepared by heating iron in an excess of bromine vapor. In its properties it closely resembles the chloride.

Ferric iodide has not been obtained. It appears, however, to be capable of existing at higher temperatures. When the heated mass which is obtained in the preparation of ferrous iodide (p. 656), and which remains after all the vapors of iodine have been expelled, is allowed to cool, it suddenly evolves, at a temperature somewhat below redness, large quantities of iodine vapor, a phenomenon which is probably due to the decomposition of ferric iodide contained in the mass.

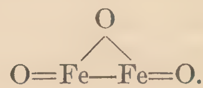
Ferric fluoride, $'\mathbf{Fe}_2F_6$, is formed when ferric oxide is dissolved in hydrofluoric acid. It forms colorless sparingly soluble crystals of the formula $'\mathbf{Fe}_2F_6,9\mathbf{O}H_2$. By heating these in a platinum crucible over the blowpipe, the water of crystallization is expelled, and the anhydrous fluoride is obtained as a fused mass. It sublimes in small transparent almost colorless cubes, isomorphous with aluminic fluoride.

COMPOUNDS OF IRON WITH OXYGEN.

Ferrous oxide, ... $\mathbf{Fe}O$.

Ferrous diferric tetroxide (*Magnetic oxide*), . . $\left\{\begin{matrix}\mathbf{Fe}O\\\mathbf{Fe}O\end{matrix}\right.Feo''$.

Ferric oxide, ... $\left\{\begin{matrix}\mathbf{Fe}O\\\mathbf{Fe}O\end{matrix}\right.O$.



Ferrous oxide, $\mathbf{Fe}O$, is difficult to prepare in a state of purity. It is obtained as a black powder by heating ferric oxide to redness in a mixture of equal volumes of carbonic anhydride and carbonic oxide, or by heating ferric oxide to 300° C. (572° F.) in a current of hydrogen. The product obtained by the latter method undergoes oxidation with incandescence if exposed to air when freshly prepared, but loses this pyrophoric property after remaining for twelve hours at ordinary temperatures in an atmosphere of hydrogen.

Ferrous hydrate, $\mathbf{Fe}Ho_2$, is formed when caustic alkali is added to the solution of a ferrous salt. The precipitation, washing and drying must be performed in an atmosphere free from oxygen. When pure it forms a white powder, but generally has a greenish tint, owing to the difficulty of entirely excluding oxygen. When exposed to the air it rapidly absorbs oxygen, and is converted into ferric oxide, sometimes with incandescence.

FERROUS DIFERRIC TETROXIDE (*Magnetic oxide*), $'\mathbf{Fe}_2O_2Feo''$.—This compound occurs native in black lustrous octahedra and other forms belonging to the regular system, more frequently, however, in granular masses, constituting the mineral *magnetic iron ore*. It is formed when iron is heated in steam or carbonic anhydride, with liberation of hydrogen and formation of carbonic oxide respectively. On the other hand, by precisely the reverse reactions, hydrogen and carbonic oxide reduce heated oxides of iron to the metallic state. When iron is heated in air it becomes coated with magnetic oxide in the form of so-called *iron scale* or *smithy scales*. This is not, however, a pure compound: the outer portions approximate more in composition to ferric oxide, $'\mathbf{Fe}_2O_3$, the inner portions, which are next the metal, to that of ferrous oxide. Ferrous diferric tetroxide is attracted by the magnet,

and the native variety frequently possesses the property of attracting iron. This naturally magnetic variety of the mineral is known as *loadstone*, and its magnetism is derived from that of the earth.

FERRIC OXIDE, $'\mathbf{Fe}_2O_3$, occurs as *specular iron ore* in lustrous steel-gray hexagonal crystals, also massive, as the important iron ore *red hæmatite*. It may be obtained artificially in reddish-brown lustrous scales by carefully heating a mixture of ferrous sulphate and common salt, extracting the mass with water:

$$\underset{\text{Ferrous sulphate.}}{2\mathbf{S}O_2\mathbf{Fe}o''} = \underset{\text{Ferric oxide.}}{'\mathbf{Fe}_2O_3} + \underset{\text{Sulphurous anhydride.}}{\mathbf{S}O_2} + \underset{\text{Sulphuric anhydride.}}{\mathbf{S}O_3}.$$

The same compound is obtained in the amorphous condition as a reddish powder by heating ferric hydrate or ferrous sulphate alone. The native oxide and the strongly ignited amorphous oxide dissolve with great difficulty in acids. Amorphous ferric oxide, obtained as a by-product in the manufacture of fuming sulphuric acid (p. 274), is employed as a red pigment under the name of *rouge*. It is also used in polishing jewellers' goods and metallic surfaces generally.

FERRIC HYDRATE, $'\mathbf{Fe}_2Ho_6$, is obtained as a bulky reddish-brown precipitate by adding ammonia to a solution of ferric chloride. When dried at ordinary temperatures it has the composition represented by the above formula, but when heated to 100° C., or when boiled with water, or even when left for a long time in contact with water, it undergoes partial dehydration, and is converted into the compounds of the formulæ $\left\{\begin{matrix}\mathbf{Fe}Ho_2\\ \mathbf{Fe}Ho_2\end{matrix}\right. O$ and $\left\{\begin{matrix}\mathbf{Fe}OHo\\ \mathbf{Fe}OHo\end{matrix}\right.$. Hydrates of this composition occur in nature as *needle iron ore* or *brown iron ore*. Ordinary iron rust has the composition $\left\{\begin{matrix}\mathbf{Fe}OHo\\ \mathbf{Fe}Ho_2\\ O\\ \mathbf{Fe}Ho_2\\ \mathbf{Fe}OHo\end{matrix}\right.$, and this compound also occurs in nature as *brown hæmatite*.

Various other complex hydrates occur as well-characterized minerals. A *soluble ferric hydrate* is also known. Thus a solution of ferric chloride dissolves large quantities of freshly precipitated ferric hydrate, yielding a dark-red liquid. The same solution may be obtained by adding ammonic carbonate to a solution of ferric chloride until a point is reached at which the precipitate of ferric hydrate no longer redissolves. If either of these solutions be subjected to dialysis, ferric chloride passes through the dialyser and a dark-red liquid remains, containing only 1.5 per cent. of hydrochloric acid to 98.5 of ferric oxide. Traces of alkalies and salts cause the solution to coagulate. All the ferric hydrates are converted on heating into ferric oxide.

OXY-SALTS OF IRON.

a. Ferrous Salts.

Ferrous nitrate, $N_2O_4Feo'',6OH_2$, is best prepared by decomposing ferrous sulphate with baric nitrate. Crystals can be obtained only from well-cooled solutions. The crystals are very unstable, and by exposure to air are speedily converted into a reddish-brown powder.

FERROUS CARBONATE, $COFeo''$, occurs native as *spathose iron ore* in rhombohedral crystals, which, however, generally contain varying quantities of the isomorphous carbonates of calcium, magnesium, and manganese. This compound may be obtained artificially in microscopic rhombohedra by heating a solution of ferrous sulphate with an excess of hydric sodic carbonate in sealed tubes to 150° C. (302° F.). Alkaline carbonates produce in solutions of ferrous salts a white precipitate of ferrous carbonate, which speedily becomes dark-colored from oxidation, and when exposed to air is eventually transformed into ferric hydrate with evolution of carbonic anhydride. Ferrous carbonate is soluble in water containing carbonic anhydride. It is in this form that iron usually occurs in chalybeate springs.

FERROUS SULPHATE (*Green vitriol*), $SOHo_2Feo'',6OH_2$.—This salt is prepared on a large scale by exposing moistened iron pyrites, FeS''_2, to the air. The soluble ferrous sulphate, together with the excess of sulphuric acid, thus formed, runs off into tanks, where the excess of acid is also converted into ferrous sulphate by the addition of scrap iron. It is best prepared in a state of purity by dissolving pure iron wire in sulphuric acid, employing an excess of the metal. It forms large pale-green monoclinic crystals, which effloresce in dry air. These are soluble in $1\frac{1}{2}$ times their weight of water at ordinary temperatures, and in $\frac{1}{3}$ of their weight of boiling water. The salt loses its 6 molecules of water of crystallization at 100° C.; at 300° C. (572° F.) it parts with its water of constitution, leaving white anhydrous SO_2Feo''. The anhydrous salt is decomposed when heated to redness, yielding ferric oxide, together with sulphurous and sulphuric anhydrides (p. 658). The moist salt absorbs oxygen from the air and turns brown. Ferrous sulphate also crystallizes in the rhombic forms of zincic sulphate. Crystals of this form may be obtained by introducing a small crystal of zincic sulphate into a supersaturated solution of ferrous sulphate. If, on the other hand, a crystal of cupric sulphate be employed to start the crystallization, triclinic crystals of the formula $SOHo_2Feo''$, $4OH_2$, isomorphous with those of cupric sulphate, are obtained. Ferrous sulphate crystallizes in all proportions with sulphates of copper, zinc, manganese, and the other metals of the isomorphous dyadic group, and cannot be purified by crystallization if any of these are present. Ferrous sulphate is employed in the preparation of inks, iron mordants, etc.—Ferrous sulphate forms, with the sulphates of the alkalies, double sulphates isomorphous with the double sulphates of the metals of the magnesium group with the alkalies. *Ammonic ferrous sulphate*, $\left\{\begin{matrix} SO_2Amo \\ Feo'' \\ SO_2Amo \end{matrix}\right.,6OH_2$, is obtained by dissolving equivalent quantities of fer-

rous sulphate and ammonic sulphate in a small quantity of hot water and allowing the solution to crystallize. It forms transparent bluish-green monoclinic crystals. It is much more permanent in air than ferrous sulphate, and for this reason is largely used instead of this salt in volumetric analysis.

Ferrous phosphate, $\mathbf{P}_2\mathrm{O}_2\mathrm{Feo}''_3,8\mathbf{O}\mathrm{H}_2$.—This compound occurs as the mineral *vivianite* in thin monoclinic prisms, generally of bluish-green tint. It is precipitated on the addition of hydric disodic phosphate to a solution of ferrous sulphate as a white amorphous powder which rapidly becomes blue from oxidation.

Ferrous silicate, $\mathbf{Si}\mathrm{Feo}''_2$, occurs native as the mineral *fayalite*. It also forms the chief constituent of *refinery-slag*, obtained in the process of refining iron previous to puddling. It also occurs in combination with other silicates in a great variety of minerals.

b. Ferric Salts.

Ferric nitrate, $\mathbf{N}_6\mathrm{O}_{12}\,('\mathrm{Fe}'''_2\mathrm{O}_6)^{vi}$, is obtained by dissolving iron in an excess of nitric acid, and carefully evaporating the solution. On adding nitric acid, crystals of the nitrate are deposited, sometimes with 12, sometimes with 18 aq., according to the concentration of the solution and the quantity of nitric acid employed. The crystals are deliquescent and readily soluble in water, but only sparingly soluble in nitric acid. The brown aqueous solution is decomposed on boiling, with separation of brown insoluble basic nitrates. Ferric nitrate is employed as a mordant.

Ferric sulphate, $\left.\begin{matrix}\mathbf{S}\mathrm{O}_2- \\ \mathbf{S}\mathrm{O}_2- \\ \mathbf{S}\mathrm{O}_2-\end{matrix}\right]('\mathrm{Fe}'''_2\mathrm{O}_6)^{vi},9\mathbf{O}\mathrm{H}_2$, occurs native in hexagonal crystals as the mineral *coquimbite*. It is best prepared by dissolving 10 parts of ferrous sulphate in water, together with 4 parts of concentrated sulphuric acid, and adding to the hot solution small quantities of nitric acid until a portion on testing with potassic ferri-cyanide no longer gives a blue precipitate. The reaction is as follows:

$$\underset{\text{Ferrous sulphate.}}{6\mathbf{S}\mathrm{O}_2\mathrm{Feo}''} + \underset{\text{Sulphuric acid.}}{3\mathbf{S}\mathrm{O}_2\mathrm{Ho}_2} + \underset{\text{Nitric acid.}}{2\mathbf{N}\mathrm{O}_2\mathrm{Ho}} = \underset{\text{Ferric sulphate.}}{3\mathbf{S}_3\mathrm{O}_6('\mathrm{Fe}'''_2\mathrm{O}_6)^{vi}} + \underset{\text{Nitric oxide.}}{2'\mathbf{N}''\mathrm{O}} + \underset{\text{Water.}}{4\mathbf{O}\mathrm{H}_2}.$$

By evaporation the anhydrous salt is obtained as a white mass. It is soluble in water, yielding a brown solution, but insoluble in concentrated sulphuric acid. Basic ferric sulphates of varying composition are obtained by boiling the dilute solution of ferric sulphate or by adding to its solution a quantity of alkali insufficient for complete precipitation.

Dipotassic diferric tetrasulphate (*Iron alum*),

$$\left.\begin{matrix}\mathbf{S}\mathrm{O}_2\mathrm{Ko} \\ \mathbf{S}\mathrm{O}_2- \\ \mathbf{S}\mathrm{O}_2- \\ \mathbf{S}\mathrm{O}_2\mathrm{Ko}\end{matrix}\right]('\mathrm{Fe}'''_2\mathrm{O}_6)^{vi},24\mathbf{O}\mathrm{H}_2.—$$

This compound is obtained when the calculated quantity of potassic sulphate is dissolved in a solution of ferric sulphate, and the concen-

trated solution is kept at a temperature of 0° C. The alum is deposited in violet octahedra, soluble in 5 parts of water at ordinary temperatures.

Ferric phosphate, $P_2O_2('Fe'''_2O_6)^{vi}$,$4OH_2$, is obtained as a white precipitate when hydric disodic phosphate is added to a solution of ferric chloride. It is insoluble in water and in acetic acid, but soluble in mineral acids.

Ferric silicates.—A *dihydric diferric disilicate*, $\begin{matrix}SiHo\\SiHo\end{matrix}('Fe'''_2O_6)^{vi}$ occurs native as the mineral *anthrosiderite*. Ferric silicates also occur in combination with other silicates in a large number of minerals.

THE FERRATES.

Neither ferric acid, FeO_2Ho_2, nor its anhydride, FeO_3, is known. When ferric acid is liberated from its salts, it is instantaneously decomposed into ferric hydrate and free oxygen.

Potassic ferrate, FeO_2Ko_2.—This compound is prepared by suspending freshly precipitated ferric hydrate in caustic potash and passing a rapid current of chlorine through the liquid, care being taken, however, that the temperature does not rise above 40° C. (104° F.). It is also formed when a positive electrode of cast iron is employed in the electrolysis of caustic potash, and when finely divided iron is fused with nitre. It forms small dark-red crystals, which appear almost black by reflected light. It dissolves in water, yielding a red solution which on standing deposits ferric hydrate and becomes colorless, oxygen being evolved. The same change takes place instantaneously on heating.

Sodic ferrate, FeO_2Nao_2, is prepared like the potash salt, which it closely resembles.

Baric ferrate, FeO_2Bao'', is obtained as a red insoluble precipitate when baric chloride is added to the solution of the potash salt. It is moderately stable and may be heated to 100° C. without decomposition.

COMPOUNDS OF IRON WITH SULPHUR.

FERROUS SULPHIDE, FeS'', is formed by the direct union of its elements. Red-hot wrought iron or steel, but not cast iron, undergoes apparent fusion when brought in contact with a roll of sulphur, owing to the formation of the more fusible monosulphide. The same compound is formed with evolution of heat when a mixture of iron filings and sulphur is moistened with water and allowed to stand at ordinary temperatures. It is best prepared by throwing a mixture of 3 parts of iron filings and 2 parts of sulphur in small portions at a time into a red hot Hessian crucible. It is thus obtained as a black porous mass, which at a higher temperature fuses, solidifying to a grayish-yellow, crystalline, metallic mass, of sp. gr. 4.79. The alkaline sulphides precipitate from solutions of ferrous or ferric salts black amorphous ferrous sulphide. In this form it is readily oxidized if exposed to the air in a moist state. Dilute hydrochloric or sulphuric acid dissolves ferrous sulphide with evolution of sulphuretted hydrogen.

Diferric trisulphide, $\left\{\begin{matrix}FeS''\\FeS''\end{matrix}\right.S''$.—This compound cannot be prepared by precipitating a ferric salt with ammonic sulphide, as under

these circumstances a mixture of ferrous sulphide with sulphur is obtained. It is formed when iron is heated with its own weight of sulphur, avoiding too high a temperature. It is thus obtained as a yellowish metallic mass of sp. gr. 4.41. This compound may be regarded as the sulphanhydride of the sulpho-acid, $\left\{\begin{matrix}FeS''Hs\\FeS''Hs\end{matrix}\right.$. This acid is not known, but its salts have been prepared. Thus *potassic sulphoferrite*, $\left\{\begin{matrix}FeS''Ks\\FeS''Ks\end{matrix}\right.$, is obtained in the form of red, lustrous, flexible needles when a mixture of 1 part of finely-divided iron, 6 parts of dry potassic carbonate, and 6 parts of sulphur is fused and the cooled mass extracted with water. *Copper pyrites*, $\left\{\begin{matrix}FeS''\\FeS''\end{matrix}\right.('Cu'_2S''_2)''$, is the cuprous salt of this sulpho-acid *Heptaferric octosulphide* (*Magnetic pyrites*), Fe_7S_8, occurs native in brownish-yellow metallic, hexagonal crystals, more frequently, however, massive. This substance is attracted by the magnet, and is sometimes itself magnetic.

Ferric Disulphide, FeS''_2.—This compound occurs native in two distinct forms. As *iron pyrites* it is found in large quantities, either massive or in brass yellow crystals belonging to the regular system. It has a specific gravity of 5.185. The same compound is obtained artificially by heating finely-divided iron with excess of sulphur to a temperature below redness. The native compound appears to have been formed by the reducing action of organic matter upon ferrous sulphate dissolved in water, and hence it is chiefly found along with the remains of organic matter such as coal, peat, etc. Sometimes it assumes the form of the piece of organic matter by which the reduction has been effected: thus wood, roots, ammonites, and other organized forms are found accurately reproduced in this material. *Marcasite*, or *radiated pyrites*, the second form of ferric disulphide, occurs in pale brass-yellow rhombic crystals with a sp. gr. of 4.68 to 4.85. Neither of the forms of iron pyrites is magnetic. It is not attacked by dilute acids or by cold concentrated sulphuric acid; but hot concentrated sulphuric acid slowly dissolves it with evolution of sulphurous anhydride. Hot nitric acid also oxidizes and dissolves it. When heated in a current of hydrogen it is reduced to the monosulphide. It burns with a flame when heated in air, yielding sulphurous anhydride and ferric oxide. In this way it is employed in enormous quantities in the manufacture of sulphuric acid.

General Properties and Reactions of the Compounds of Iron:

a. *Ferrous salts*.—The aquates of these salts are green, the anhydrous salts are white. *Caustic alkalies* precipitate white ferrous hydrate, which speedily oxidizes by exposure to the air and becomes green. *Ammonia* only partially precipitates solutions of ferrous salts as hydrate; in presence of an excess of ammonic chloride no precipitate is produced by ammonia, but the ammoniacal solution absorbs oxygen from the air, and a film of ferric hydrate forms upon the surface. *Sulphuretted hydrogen* does not precipitate ferrous salts in acid solution; *ammonic sulphide* precipitates black hydrated ferrous sulphide, which is readily oxidized

by exposure to air. *Potassic ferrocyanide* gives a white precipitate of dipotassic ferrous ferrocyanide ($Fe''Cy_6Fe''K_2$), which rapidly oxidizes and becomes blue. *Potassic ferricyanide* occasions a deep-blue precipitate of ferrous ferricyanide (Turnbull's blue) ($Fe''_3{}'Fe'''_2Cy_{12}$). Oxidizing agents convert the ferrous into ferric salts.

b. *Ferric salts.*—These have a yellow or reddish-brown color. *Caustic alkalies* and *ammonia* give a reddish-brown bulky precipitate of ferric hydrate, insoluble in excess. *Sulphuretted hydrogen* does not precipitate the iron but reduces it to the ferrous state, whilst finely divided white sulphur is deposited. *Ammonic sulphide* precipitates black ferrous sulphide with separation of sulphur. *Potassic ferrocyanide* gives a deep-blue precipitate of ferric ferrocyanide (Prussian blue) ($3Fe''Cy_2,2'Fe'''_2Cy_6$). *Potassic ferricyanide* gives no precipitate with solutions of ferric salts; but the color of the liquid changes from yellow to reddish-brown. Soluble *thiocyanates* give a blood-red coloration which is not destroyed by hydrochloric acid. *Baric carbonate* precipitates the whole of the iron in the cold as ferric hydrate with evolution of carbonic anhydride. *Sodic acetate* colors neutral solutions dark-red, and, on boiling, the whole of the iron is precipated as basic ferric acetate. The *benzoates* and *succinates* of the alkali-metals produce in neutral solutions bulky insoluble brown precipitates.

All compounds of iron when heated with sodic carbonate on charcoal in the reducing flame yield a black magnetic powder. Borax and microcosmic salt give with iron compounds beads which in the reducing flame are bottle-green and in the oxidizing flame yellow, or, if the quantity of iron is very small, colorless. The compounds of iron do not color flame. The spark-spectrum of the metal contains many hundreds of bright lines coincident with lines of the solar spectrum.

COBALT, Co.

Atomic weight = 58.6. *Molecular weight unknown.* *Sp. gr.* 8.5 *to* 8.7. *Atomicity*'', ^{iv}, *and* ^{vi}? *Also a pseudo-triad.* *Evidence of atomicity:*

Cobaltous chloride,	$Co''Cl_2$.
Cobaltic disulphide,	$Co^{iv}S''_2$.
Cobaltic oxide,	$\left\{\begin{matrix} Co'''O \\ Co'''O \end{matrix}\right. O$.

History.—Cobalt was discovered by Brandt in 1735.

Occurrence.—Metallic cobalt occurs in small quantity in meteoric iron. Its chief ores, which are not very widely distributed, are the arsenides and arsenical sulphides, such as *speiss-cobalt*, $''\left\{\begin{matrix} As \\ As \end{matrix}\right. Co''$, and *glance-cobalt*, $\left\{\begin{matrix} As \\ As \end{matrix}\right. (Co''S'')''_2$. In almost all the cobalt minerals a portion of cobalt is replaced by nickel, iron, and other isomorphous metals. Cobalt is present in the solar atmosphere.

Extraction.—The ores of cobalt, which consist, as above stated, of mixed arsenides and sulphides of cobalt, nickel, and iron, and generally contain, in addition, copper, bismuth, and other metals, are first roasted

in a current of air. In this way an impure cobaltous arsenate, known as *zaffre*, is obtained, whilst large quantities of arsenious anhydride are volatilized, this product being carefully condensed. The roasted mass is extracted with hydrochloric acid until the residue is free from cobalt. On evaporating the solution chlorine is evolved, the arsenic acid being reduced by the hydrochloric acid to arsenious acid, which crystallizes out. The remainder of the arsenic is got rid of by oxidizing the arsenious acid back to arsenic acid by the addition of bleaching powder, carefully avoiding an excess, and then *exactly* neutralizing with milk of lime. In this way ferric hydrate is precipitated, carrying with it all the arsenic acid. The solution is then again acidified with hydrochloric acid and treated with sulphuretted hydrogen in order to precipitate copper, bismuth, etc. The cobalt is then precipitated from the weak acid solution as cobaltic oxide, by the careful addition of bleaching powder. An excess of the precipitant is to be avoided, as this would bring down the nickel. The crude oxide, which still contains nickel and iron, is washed and ignited. It is thus converted into cobaltous dicobaltic tetroxide, $\left\{ \begin{matrix} \mathrm{CoO} \\ \mathrm{CoO} \end{matrix} \right. \mathrm{Coo}''$, in which form it is used in imparting a blue color to glass and porcelain. In order to obtain pure metallic cobalt, the commercial oxide is dissolved in hydrochloric acid, and the solution evaporated to a small bulk. Ammonic chloride and an excess of ammonia are then added. Any ferric hydrate which is precipitated is filtered off, and the solution is exposed to the air for some days until a portion of the liquid, when treated with excess of concentrated hydrochloric acid, does not become blue. Excess of concentrated hydrochloric acid is then added to the entire liquid, which is now heated to boiling and evaporated. Almost the whole of the cobalt separates as *purpureo-cobalt chloride*, Co_2Cl_6,-$(NH_3)_{10}$, in the form of a red crystalline powder. This, when heated in a current of hydrogen, is reduced to spongy metallic cobalt, which may be obtained in the form of a regulus by fusion in a crucible of lime or graphite. The oxides of cobalt are also reduced to the metallic state when heated in a current of hydrogen.

Properties.—Metallic cobalt is almost white, with a faint reddish tinge, and is capable of taking a high polish. It is malleable and very tenacious. It is magnetic, and, unlike iron and nickel, is attracted by the magnet also when red hot. Its fusing-point lies somewhat lower than that of iron. The compact metal is oxidized neither in air nor in water at ordinary temperatures; but when heated in air it undergoes slow oxidation. It dissolves slowly in dilute sulphuric and hydrochloric acids with evolution of hydrogen, and is readily soluble in dilute nitric acid.

COMPOUNDS OF COBALT WITH THE HALOGEN.

Cobaltous chloride, $CoCl_2$, is obtained by dissolving any of the oxides of cobalt in hydrochloric acid and evaporating. In the case of the oxides higher than cobaltous oxide the solution evolves chlorine. The concentrated liquid deposits dark-red monoclinic crystals of the formula $CoCl_2,6OH_2$. These, when heated to 120° C. (248° F.), are

converted into a dark-blue crystalline powder possessing the formula $CoCl_2,2OH_2$, and at a temperature above 140° C. (284° F.), this salt becomes anhydrous. The anhydrous salt sublimes in a current of chlorine, yielding dark-blue scales, which, when exposed to air, absorb moisture and become pink-colored. The anhydrous chloride dissolves slowly in water, yielding a pink-colored solution, and in absolute alcohol with a blue color, which becomes pink on the addition of water. Most cobaltous salts exhibit this property of possessing a pink or rose-color in the highly hydrated condition, and a blue or violet color in the slightly hydrated or anhydrous condition. Owing to this property a solution of a cobaltous salt may be employed as a so-called sympathetic ink. Characters inscribed upon paper with a dilute solution of cobaltous chloride are invisible under ordinary conditions, but appear blue when the paper is warmed to expel the moisture, gradually disappearing again on cooling, owing to the absorption of moisture from the air. In like manner a not too dilute pink-colored solution of cobaltous chloride becomes blue on the addition of an excess of strong hydrochloric acid, owing to the abstraction of water from the salt in solution.

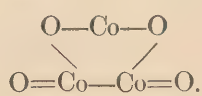
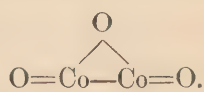
Cobaltic chloride, $'Co_2Cl_6$, is probably formed when cobaltic oxide is dissolved in cold hydrochloric acid, but the solution speedily evolves chlorine, and contains cobaltous chloride.

Cobaltous bromide, $CoBr_2$, resembles the chloride in properties and mode of preparation. The aquate, $CoBr_2,6OH_2$, is dark-red, the anhydrous salt green.

Cobaltous iodide, CoI_2.—This compound is obtained by digesting finely divided cobalt with iodine and water. It forms either brownish-red prisms of the formula $CoI_2,6OH_2$, or small green very deliquescent crystals of the formula $CoI_2.2OH_2$. When heated to 130° C. (266° F.), the salt is converted into a black graphite-like mass of the anhydrous iodide.

Cobaltous fluoride, $CoF_2,2OH_2$, is obtained in rose-red crystals by dissolving the carbonate in hydrofluoric acid and evaporating the solution.

COMPOUNDS OF COBALT WITH OXYGEN.

Cobaltous oxide, . .	CoO.	
Cobaltous dicobaltic tetroxide, ...	$\left\{\begin{matrix} CoO \\ CoO \end{matrix}\right\} Coo''$.	
Cobaltic oxide, . . .	$\left\{\begin{matrix} CoO \\ CoO \end{matrix}\right\} O$.	

Cobaltous oxide, CoO, is formed when cobaltous hydrate or cobaltous carbonate is heated with careful exclusion of air. It is best prepared by strongly heating either of the higher oxides in a current of carbonic anhydride. It forms a greenish-brown powder, readily soluble in acids. When heated in hydrogen or carbonic oxide it is reduced to metal.

Cobaltous hydrate, $CoHo_2$.—On the addition of a caustic alkali to the solution of a cobaltous salt a blue basic salt is precipitated, which on boiling is converted into the rose-red hydrate. This, on exposure to air, speedily turns brown from oxidation. It is insoluble in caustic alkalies, but dissolves in ammonia with a reddish color.

Cobaltous dicobaltic tetroxide, $'\mathbf{Co}_2O_2Coo''$.—This compound is formed when either of the other oxides, or cobaltous nitrate, is strongly ignited in air. It forms a black non-magnetic powder.

Cobaltic oxide, $'\mathbf{Co}_2O_3$, is prepared by gently igniting cobaltous nitrate. It is a dark-brown powder which dissolves in cold acids, yielding brown solutions of unstable cobaltic salts. On warming or evaporating the solutions decomposition ensues—in the case of the hydracids with evolution of halogen, in the case of the oxy-acids with evolution of oxygen—and a cobaltous salt remains in solution.

Cobaltic hydrate, $'\mathbf{Co}_2Ho_6$, is obtained as a black amorphous precipitate by adding an alkaline hypochlorite to the solution of a cobaltous salt. It behaves towards acids like cobaltic oxide.

OXY-SALTS OF COBALT.

Cobaltous nitrate, $\mathbf{N}_2O_4Coo'',6\mathbf{O}H_2$, forms red, very soluble deliquescent monoclinic prisms.

Cobaltous carbonate, $\mathbf{C}OCoo''$.—The anhydrous salt is obtained in bright-red microscopic octahedra by heating cobaltous chloride to 140° C. (284° F.) with a solution of hydric sodic carbonate which has been previously saturated with carbonic anhydride. An aquate of the formula $\mathbf{C}OCoo''_2,6\mathbf{O}H_2$ is prepared by mixing a solution of cobaltous nitrate with the above solution of hydric sodic carbonate saturated with carbonic anhydride, and exposing the mixture for some time to a low temperature.—Normal alkaline carbonates precipitate from solutions of cobaltous salts blue or violet basic carbonates.

Cobaltous sulphate, $\mathbf{S}O_2Coo''$.—This salt is prepared by dissolving the oxide, hydrate, or carbonate in sulphuric acid. Its solutions deposit at ordinary temperatures dark-red monoclinic crystals of *dihydric cobaltous sulphate*, $\mathbf{S}OHo_2Coo'',6\mathbf{O}H_2$, isomorphous with ferrous sulphate. The same salt occurs native as *cobalt vitriol*. Various other aquates are known.—Cobaltous sulphate forms with the sulphates of the alkalies double salts, which correspond exactly with the double sulphates of zinc, magnesia, etc., with the alkalies. Thus, *dipotassic cobaltous sulphate*, $\begin{matrix}\mathbf{S}O_2Ko\\ \mathbf{S}O_2Ko\end{matrix}Coo'',6\mathbf{O}H_2$, forms monoclinic crystals.

Cobaltous phosphate.—The normal salt, $\mathbf{P}_2O_2Coo''_3$, is obtained as a rose-red hydrated precipitate when hydric disodic phosphate is added to the solution of a cobaltous salt. —*Hydric cobaltous phosphate*, $2\mathbf{P}OHoCoo'',5\mathbf{O}H_2$, is prepared by dividing a quantity of the foregoing salt into two equal portions, dissolving the one portion in the smallest possible quantity of hydrochloric acid and then adding the other. It forms thin violet laminæ.

Cobaltous arsenate.—The normal salt, $\mathbf{As}_2O_2Coo''_3,8\mathbf{O}H_2$, occurs native as *cobalt-bloom* or *erythrine* in peach-blossom-colored needles, or in earthy incrustations. This mineral has been formed by the spontaneous oxidation of speiss-cobalt and other native arsenites of cobalt. *Zaffre* is an impure basic arsenate of cobalt, prepared by roasting speiss-cobalt. It is employed in painting on glass and porcelain, for which purpose it must be free from iron.

Silicates of Cobalt.—These have not been prepared in a state of purity. When an alkaline silicate is added to the solution of a cobaltous salt a blue hydrated silicate of cobalt is precipitated. *Smalt* is a cobalt-potash glass—a mixed silicate of cobalt and potassium. In a finely ground condition it is employed as a blue pigment. It is prepared on a large

scale from speiss-cobalt or cobalt-glance. The ore is roasted at a low temperature, so as to oxidize the cobalt, leaving the nickel, iron, and other impurities, the presence of which would be detrimental to the purity of color of the smalt, as far as possible unaltered. The roasted ore is then fused with quartz-sand and potashes. The oxidized cobalt is taken up by the silica and unites with the potassic silicate to form smalt, whilst the nickel, iron, copper, bismuth, arsenic, etc., collect as a regulus at the bottom of the melting-pot. The glass is then finely ground under water. It contains from 6 to 7 per cent. of cobalt and from 60 to 70 per cent. of silica. Smalt is less frequently employed as a pigment than formerly, owing to the introduction of artificial ultramarine; but it possesses the advantage over the latter pigment of not being altered by acids.

Two other cobalt pigments are also manufactured: *Thenard's blue* or *cobalt ultramarine*, which is obtained by precipitating mixed solutions of alum and cobaltous sulphate with sodic carbonate and igniting the precipitate; and *Rinmann's green*, which is prepared in a similar manner by igniting the precipitate produced by sodic carbonate in mixed solutions of cobaltous sulphate and zincic sulphate. Nothing is known concerning the constitution of these pigments.

It has already been mentioned (p. 666) that the simple cobaltic salts are capable of existing only in solution. Double cobaltic salts are, however, known which possess a considerable degree of stability.

Potassic cobaltic nitrite, $\mathbf{N}_6O_6('Co'''_2O_6)^{vi},6\mathbf{N}OKo$.—This salt is formed as a yellow crystalline precipitate when potassic nitrite is added to the solution of a cobaltous salt acidified with acetic acid. Nitric oxide is evolved in the reaction:

$$\underset{\text{Cobaltous chloride.}}{2\mathbf{Co}Cl_2} + \underset{\text{Potassic nitrite.}}{10\mathbf{N}OKo} + \underset{\text{Nitrous acid.}}{4\mathbf{N}OHo} = \underset{\text{Potassic cobaltic nitrite.}}{\mathbf{N}_6O_6('Co'''_2O_6)^{vi},6\mathbf{N}OKo}$$

$$+ \underset{\text{Potassic chloride.}}{4KCl} + \underset{\text{Nitric oxide.}}{2'\mathbf{N}''O} + \underset{\text{Water.}}{2\mathbf{O}H_2}.$$

COMPOUNDS OF COBALT WITH SULPHUR.

COBALTOUS SULPHIDE, $\mathbf{Co}S''$, is formed as a gray, metallic, crystalline mass when cobalt is fused with sulphur. It may be obtained in long, thin, very lustrous needles of a yellowish-gray color by fusing a mixture of anhydrous cobaltous sulphate and baric sulphide with an excess of sodic chloride. Ammonic sulphide precipitates from solutions of cobaltous salts black amorphous hydrated cobaltous sulphide, scarcely soluble in cold dilute hydrochloric acid. Concentrated hydrochloric acid dissolves it with evolution of sulphuretted hydrogen.

Other sulphides, $'\mathbf{Co}_2S''_3$ and $\mathbf{Co}S''_2$, are obtained by heating cobaltous sulphide with sulphur in a current of hydrogen.

Cobaltous dicobaltic tetrasulphide, $\mathbf{Co}_2S''_2Cos''$, occurs native in steel-gray or copper-red regular octahedra as the mineral *cobalt pyrites*.

AMMONIUM COMPOUNDS OF COBALT (COBALTAMINES).

The cobaltamines are of two classes—cobaltous and cobaltic. Their salts possess the empirical composition of additive compounds of one molecule of a cobaltous or a cobaltic salt with a certain number of molecules of ammonia. The salts of the first class are formed by the direct union of gaseous ammonia with anhydrous cobaltous salts. In the formation of the cobaltamines of the second class the oxygen of the air also plays a part. Thus the solution of a cobaltous salt in aqueous ammonia rapidly absorbs oxygen and is converted into a cobaltic ammonium base. Various bases belonging to this class are known. They all possess characteristic colors, and from these their names are derived.

a. Cobaltous Ammonium Compounds.

Cobaltosammonic chlorides.—Anhydrous cobaltous chloride absorbs dry ammonia gas, and is converted into the compound $CoCl_2,6NH_3 = \left\{\begin{array}{l} NH_3Cl \\ NH_3 \\ NH_3 \\ Co'' \\ NH_3 \\ NH_3 \\ NH_3Cl \end{array}\right.$, which is thus obtained as a pale pink powder. The same compound is deposited in red octahedral crystals when the chloride is dissolved in concentrated aqueous ammonia and the solution allowed to stand in a well-stoppered bottle. When heated to 120° C. (248° F.) it parts with four molecules of ammonia and is converted into *cobaltoso-diammonic dichloride*, $\left\{\begin{array}{l} NH_3Cl \\ Co'' \\ NH_3Cl \end{array}\right.$.

A nitrate of the empirical formula $N_2O_2Coo'',6NH_3,2OH_2$, and a sulphate, $SO_2Coo'',6NH_3$, have also been prepared.

b. Cobaltic Ammonium Compounds.

These may be divided into four principal series, of which the chlorides may serve as examples:

	Empirical formula.
Dicobaltic-hexammonic (*dichro-cobaltic*) chloride, .	$'Co_2Cl_66NH_3$.
Dicobaltic-octammonic (*praseo-* and *fusco-cobaltic*) chloride, ...	$'Co_2Cl_6,8NH_3$.
Dicobaltic-decammonic (*roseo-* and *purpureo-cobaltic*) chloride, ...	$'Co_2Cl_6,10NH_3$.
Dicobaltic-dodecammonic (*luteo-cobaltic*) chloride,	$'Co_2Cl_6,12NH_3$.

The *color*-names (see above) are given in brackets. It will be observed that some of these bases exist in isomeric modifications.

The above compounds behave like chlorides of complex ammonium bases. Thus the chlorine may be replaced by hydroxyl, and the resulting compounds are hydrates possessing an alkaline reaction and a purely alkaline, as opposed to a metallic, taste. Again, the chlorides form double compounds with platinic and auric chlorides.

Dichro-cobaltic chloride (*Dicobaltic hexammonic chloride*) $\left\{\begin{array}{l} \quad\ulcorner NH_3Cl \\ Co-NH_3Cl \\ \quad\llcorner NH_3Cl \\ \quad\ulcorner NH_3Cl \\ Co-NH_3Cl \\ \quad\llcorner NH_3Cl \end{array}\right.,2OH_2$. — This compound is formed when a solution of cobaltous chloride in aqueous ammonia is exposed to the air until the separation of black cobaltic hydrate commences. On

adding an excess of concentrated hydrochloric acid and allowing the liquid to stand for some time, the cobaltamine chloride is deposited in dark-colored laminæ or feather-shaped crystals. The dichroism of this compound is best exhibited by breaking a large crystal; the splinters display different colors.

Praseo-cobaltic chloride,
$$\left\{\begin{array}{l} \quad -\mathbf{N}H_2(N^vH_4)Cl \\ Co-\mathbf{N}H_3Cl \\ \quad -\mathbf{N}H_3Cl \\ \quad -\mathbf{N}H_3Cl \\ Co-\mathbf{N}H_3Cl \\ \quad -\mathbf{N}H_2(N^vH_4)Cl \end{array}\right. ,2OH_2.$$
— This compound is generally formed along with the preceding and other cobaltamines, remaining in the filtrate after these have been precipitated with concentrated hydrochloric acid. On saturating the liquid with ammonic chloride the praseo-compound separates in bright-green glistening needles.

Roseo-cobaltic chloride,
$$\left\{\begin{array}{l} \quad -\mathbf{N}H_2(N^vH_4)Cl \\ Co-\mathbf{N}H_2(N^vH_4)Cl \\ \quad -\mathbf{N}H_3Cl \\ \quad -\mathbf{N}H_3Cl \\ Co-\mathbf{N}H_2(N^vH_4)Cl \\ \quad -\mathbf{N}H_2(N^vH_4)Cl \end{array}\right. ,2OH_2.$$
—If a solution of cobaltous chloride in aqueous ammonia be oxidized by exposure to the air until a sample on testing with excess of strong hydrochloric acid no longer assumes a blue color, the liquid contains the roseo-compound. This may be separated by supersaturating the solution with strong hydrochloric acid, carefully avoiding any rise of temperature when the roseo-salt is deposited as a brick-red powder. The two molecules of water, which in the above formulæ are represented as water of crystallization, are in reality water of constitution, inasmuch as they cannot be expelled without converting the compound into *purpureo-cobaltic chloride*, a salt which, though differing totally in its properties from the roseo-salt, possesses the same chemical composition, excepting that it is anhydrous. The purpureo-salt cannot be converted into the roseo-salt merely by recrystallizing from water. The dry roseo-salt slowly changes at ordinary temperatures into the purpureo-salt. This change takes place more rapidly in solutions, and on boiling is practically instantaneous.

A number of other roseo-salts have been prepared.

Purpureo-cobaltic chloride.—This compound possesses, as above stated, the same composition as the foregoing, less two molecules of water. It is obtained by the same process as the roseo-salt, except that after supersaturating with strong hydrochloric acid the liquid is heated to boiling. The red powder which separates is purified by recrystallization from hot dilute hydrochloric acid. The compound is thus obtained in small purple crystals. It may be converted into the roseo-compound by dissolving in dilute aqueous ammonia and adding the solution drop by drop to carefully-cooled strong hydrochloric acid.

The salts of the purpureo-base with the various other acids have also been prepared.

Luteo-cobaltic chloride,
$$\left\{\begin{array}{l} \quad -\mathbf{N}H_2(N^vH_4)Cl \\ Co-\mathbf{N}H_2(N^vH_4)Cl \\ \quad -\mathbf{N}H_2(N^vH_4)Cl \\ \quad -\mathbf{N}H_2(N^vH_4)Cl \\ Co-\mathbf{N}H_2(N^vH_4)Cl \\ \quad -\mathbf{N}H_2(N^vH_4)Cl \end{array}\right. .$$
—No method of preparing the luteo- or dodecamine-compounds yielding perfectly certain results has yet been discovered. They are formed along with the other cobaltamines in the oxidation of ammoniacal solutions of cobaltous salts, especially in presence of ammonic chloride, and must be separated from these by systematic crystallization. Luteo-cobaltic chloride crystallizes in reddish-yellow monoclinic prisms.

The above list includes only the principal cobaltamines. Various other complex bases of this class have been prepared.

General Properties and Reactions of the Compounds of Cobalt.—The aquates of the cobaltous salts are usually red; the anhydrous salts are blue. With *caustic alkalies* their solutions yield in the cold a blue precipitate of a basic salt, which on boiling is converted into pink cobaltous hydrate. *Ammonia* produces a similar precipitate

soluble in excess, yielding a reddish solution which absorbs oxygen from the air and becomes reddish-brown. In presence of salts of ammonia no precipitate is produced on addition of ammonia. *Sulphuretted hydrogen* gives no precipitate in presence of strong acids; *ammonic sulphide* precipitates black hydrated cobaltous sulphide, insoluble in alkalies and alkaline sulphides, scarcely soluble in dilute hydrochloric acid, readily soluble in aqua-regia. *Potassic ferrocyanide* gives a green precipitate of cobaltous ferrocyanide ($Co''_2Fe''Cy_6$), and *potassic ferricyanide* a reddish-brown precipitate of cobaltous ferricyanide (Co''_3-$'Fe'''_2Cy_{12}$). *Potassic cyanide* precipitates pale-brown cobaltous cyanide, which dissolves in an excess of the alkaline cyanide, yielding a double cyanide of potassium and cobalt. From this solution acids precipitate cobaltous cyanide. If, however, to the solution containing the double cyanide, together with an excess of potassic cyanide, a small quantity of hydrochloric acid insufficient to cause a precipitate be added, and the liquid be boiled, potassic cobalticyanide ($K_6'Co'''_2Cy_{12}$) is formed, and in the solution of this salt neither acids nor ammonic sulphide occasion a precipitate. (Distinction between the compounds of cobalt and nickel.) All the compounds of cobalt when heated with sodic carbonate on charcoal in the reducing flame yield shining white metallic particles which are attracted by a magnet. Cobalt compounds color the borax and microcosmic salt beads deep-blue, both in the oxidizing and in the reducing flame. They do not yield a flame-spectrum.

NICKEL, Ni.

Atomic weight = 58.6. *Molecular weight unknown. Sp. gr.* 8.9. *Atomicity* $''$, ^{iv}, *and* ^{vi} ? *Also a pseudo-triad. Evidence of atomicity:*

Nickelous chloride, ...	$\mathbf{Ni''Cl_2}$.
Nickelic disulphide, ...	$\mathbf{Ni^{iv}S''_2}$.
Nickelic oxide, ...	$\left\{\begin{matrix}\mathbf{Ni'''O}\\ \mathbf{Ni'''O}\end{matrix}\right.O$.

History.—Metallic nickel was first obtained by Cronstedt in 1751.

Occurrence.—Nickel occurs in the native state in meteoric iron, of which it is an invariable constituent. Its chief ores are its compounds with arsenic, antimony, and sulphur; and in these it is generally associated with cobalt. *Kupfer nickel*, so called from its copper-red color, is a dinickelous diarsenide, $\left\{\begin{matrix}\mathbf{As}Ni\\ \mathbf{As}Ni\end{matrix}\right.$; this is the most important ore of the metal. A nickelous diarsenide,'' $\left\{\begin{matrix}\mathbf{As}\\ \mathbf{As}\end{matrix}\right.Ni$, also occurs as *arsenical nickel.* Other minerals are *millerite* or *nickel blende*, a nickelous sulphide, $\mathbf{Ni}S''$; *nickel glance*, a sulph-arsenide, $\left\{\begin{matrix}\mathbf{As}\\ \mathbf{As}\end{matrix}\right.(Ni''S'')''_2$; and *breithauptite*, a dinickelous diantimonide, $\left\{\begin{matrix}\mathbf{Sb}Ni.\\ \mathbf{Sb}Ni\end{matrix}\right.$ In New Caledonia a source of nickel has lately been discovered in the mineral *garnierite*, a nickelous silicate of the formula $2\mathbf{Si}_4O_3Nio''_5,3\mathbf{O}H_2$, which occurs

there in large quantities. This ore is remarkable as being free from cobalt. Nickel has been detected in the solar atmosphere.

Extraction.—The process of extracting nickel from its ores is identical with that employed in the extraction of cobalt (p. 663) up to the point at which the cobalt is precipited as cobaltic oxide by bleaching-powder. From the solution thus freed from cobalt the nickel is precipitated as hydrate by the addition of milk of lime. The precipitate is ignited and afterwards, in order to remove the excess of lime, treated with dilute hydrochloric acid, in which the ignited oxide of nickel is insoluble. The purified oxide is reduced by heating with carbon.

Pure nickel may be prepared by heating pure nickelous oxalate with exclusion of air. The metallic powder thus obtained may be fused into a regulus in a lime crucible.

$$\underset{\text{Nickelous oxalate.}}{\left\{\begin{matrix}CO\\CO\end{matrix}\right.Nio''} = Ni + \underset{\text{Carbonic anhydride.}}{2CO_2}.$$

Properties.—Nickel is almost silver-white, with a faint yellowish tinge. It is capable of taking a high polish. It is very hard, but at the same time malleable and ductile. Nickel fuses at a somewhat lower temperature than cobalt. It is attracted by the magnet, but loses this property at a high temperature. It is not oxidized either in air or water at ordinary temperatures, and is oxidized only with difficulty when heated in air. It decomposes steam slowly at a red-heat and is converted into nickelous oxide. It dissolves slowly in dilute hydrochloric and sulphuric acids, but is readily soluble in dilute nitric acid. Concentrated nitric acid renders it "passive" like iron.

The commercial metal contains carbon along with traces of cobalt, iron, copper, and other metals. The presence of carbon has the same effect upon nickel as upon iron: it diminishes the malleability and lowers the fusing-point of the metal.

Nickel plating.—Nickel may be electrolytically deposited in a coherent coating from a solution of pure *diammonic nickelous sulphate,* $\begin{matrix}SO_2Amo\\SO_2Amo\end{matrix}Nio''$. A plate of pure nickel serves as the positive electrode. Iron and steel are frequently coated with nickel, both on account of the beauty and permanence of the metallic surface thus obtained, and also as a protection against rust.

Alloys of nickel.—Nickel yields with copper valuable alloys of a silver-white color. The material of the small coinage in the United States, in Germany, in Belgium, in Switzerland, and in Brazil, is an alloy of 1 part of nickel with 3 of copper. As this alloy is more valuable than copper, the coins are smaller and consequently more portable than copper coins possessing an equal value, whilst, owing to the hardness of the alloy, this coinage is also very durable. Chinese *packfong* is an alloy of copper, nickel, and zinc. *German silver* or *nickel silver* is a similar alloy, consisting, as a rule, of 5 parts of copper, 2 parts of nickel, and 2 parts of zinc. When first prepared it is crystalline and brittle; but by rolling and hammering, heating and allowing to cool, it is rendered tenacious and malleable.

COMPOUNDS OF NICKEL WITH THE HALOGENS.

NICKELOUS CHLORIDE, $\mathbf{Ni}Cl_2$, is obtained as a yellow earthy mass by dissolving the oxide or the carbonate in hydrochloric acid and evaporating the solution to dryness. It may be sublimed in a current of chlorine, and is thus obtained in lustrous golden-yellow laminæ. It dissolves in water, yielding a green solution which deposits on evaporation green monoclinic prisms of the formula $\mathbf{Ni}Cl_2,6\mathbf{O}H_2$.

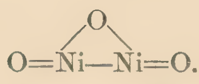
Nickelous bromide, $\mathbf{Ni}Br_2$, is prepared by heating finely divided nickel in bromine vapor. Combination occurs with incandescence, and the nickelous bromide sublimes in golden-yellow scales. The compound deliquesces in moist air. The green aqueous solution deposits on evaporation deliquescent needles of the aquate $\mathbf{Ni}Br_2,3\mathbf{O}H_2$.

Nickelous iodide, $\mathbf{Ni}I_2$, is obtained in a similar manner by heating spongy nickel in iodine vapor. It forms black lustrous laminæ which dissolve in water, yielding a green solution. The aquate $\mathbf{Ni}Br_2,6\mathbf{O}H_2$ forms bluish-green deliquescent prisms.

Nickelous fluoride, $\mathbf{Ni}F_2$, is prepared by evaporating the solution of the carbonate in hydrofluoric acid. Bluish-green crystals of the formula $\mathbf{Ni}F_2,3\mathbf{O}H_2$ are deposited, which on boiling with pure water are decomposed with separation of an insoluble oxyfluoride.

COMPOUNDS OF NICKEL WITH OXYGEN.

Nickelous oxide, . . . $\mathbf{Ni}O$

Nickelic oxide, . . . $\left\{\begin{matrix}\mathbf{Ni}O\\ \mathbf{Ni}O\end{matrix}\right. O$ 

NICKELOUS OXIDE, $\mathbf{Ni}O$, occurs native as the rare mineral *bunsenite* in green, translucent, regular octahedra. It may be obtained artificially in crystals by heating a mixture of nickelous sulphate and potassic sulphate to a high temperature. In the crystallized condition it is with difficulty attacked by acids. By igniting the hydrate or carbonate it is obtained as a gray amorphous powder, readily soluble in acids.

Nickelous hydrate, $\mathbf{Ni}Ho_2$, is an apple-green precipitate, obtained by adding caustic alkalies to the boiling solution of a nickelous salt. The precipitate is washed with hot water and dried. Acids dissolve it readily. It is insoluble in potassic hydrate and sodic hydrate, but ammonia dissolves it, yielding a blue solution, from which it is reprecipitated as a green crystalline powder on expelling the ammonia by boiling.

NICKELIC OXIDE, $'\mathbf{Ni}_2O_3$, is prepared by careful ignition of the nitrate. It is a black powder which dissolves in hydrochloric acid with evolution of chlorine, and in sulphuric acid with evolution of oxygen. Ammonia dissolves it with evolution of nitrogen.

$$\underset{\text{Nickelic oxide.}}{3'\mathbf{Ni}_2O_3} + \underset{\text{Ammonia.}}{2\mathbf{N}H_3} = \underset{\text{Nickelous hydrate.}}{6\mathbf{Ni}Ho_2} + N_2 + \underset{\text{Water.}}{3\mathbf{O}H_2}.$$

Nickelic hydrate, $'\mathbf{Ni}_2Ho_6$.—This compound is obtained as an amorphous black powder when chlorine is passed through water (or preferably through a solution of an alkaline hydrate or carbonate) in which nickelous hydrate is suspended; or by warming a solution of a nickelous salt with an alkaline hypochlorite. Towards acids and ammonia it behaves like nickelic oxide.

OXY-SALTS OF NICKEL.

Nickelous nitrate, $N_2O_4Nio'',6OH_2$, is obtained by dissolving the metal, the oxide, or the carbonate in nitric acid. It crystallizes in deliquescent green monoclinic prisms.

Nickelous nitrite, N_2O_2Nio'', is prepared by decomposing nickelous sulphate with baric nitrite and evaporating the filtrate over sulphuric acid. It forms reddish-yellow crystals, which, when dry, may be heated to 100° C. without decomposition, but in solution are decomposed at 80° C. (176° F.) with separation of a basic salt.—It forms with the nitrites of other metals double salts: thus *potassic nickelous nitrite*, N_2O_2Nio'',-$4NOKo$, and *baric nickelous nitrite*, $N_2O_2Nio'',2N_2O_2Bao''$. On adding potassic nitrite to the mixed solution of a nickel salt with a salt of barium, strontium, or calcium, the triple salts,

$$N_2O_2Nio'',N_2O_2Bao'',2NOKo\text{ ; }N_2O_2Nio'',N_2O_2Sro'',2NOKo\text{; and }N_2O_2Nio'',N_2O_2Cao'',2NOKo,$$

are precipitated as sparingly soluble yellow crystalline powders, consisting of minute octahedra. These salts closely resemble in appearance potassic cobaltic nitrite. Owing to the formation of these salts it is not possible, in presence of the metals of the alkaline earths, to separate cobalt from nickel by means of potassic nitrite.

Nickelous carbonate.—The anhydrous salt, $CONio''$, forms pale-green microscopic octahedra; the aquate, $CONio'',6OH_2$, crystallizes in minute rhombohedra or prisms Both are obtained like the corresponding cobalt compounds (p. 666).

NICKELOUS SULPHATE.—This salt is obtained by dissolving metallic nickel, or its oxide, hydrate, or carbonate, in dilute sulphuric acid. At ordinary temperatures it crystallizes from neutral solutions in green rhombic prisms of the formula $SOHo_2Nio'',6OH_2$, isomorphous with magnesic sulphate. At temperatures between 30° and 40° C. (86–104° F.), or from solutions containing an excess of acid, bluish-green quadratic pyramids of the formula $SOHo_2Nio'',5OH_2$, are obtained. This aquate is also deposited at temperatures above 50° C. (122° F.), but in monoclinic forms. 100 parts of water at 16° C. (60° F.) dissolve 37.4 parts of anhydrous salt.—Anhydrous nickelous sulphate absorbs dry ammonia and is converted into a violet-white powder of the composition $SO_2Nio'',6NH_3$.—Nickelous sulphate forms double salts with the sulphates of the alkali metals and ammonia. *Diammonic nickelous sulphate*, $\begin{matrix}SO_2Amo\\SO_2Amo\end{matrix}Nio'',6OH_2$, a salt employed in nickel electro-plating (p. 671), is prepared by adding ammonic sulphate to a concentrated solution of pure nickelous sulphate. The double salt separates as a crystalline powder and is purified by recrystallization.

Nickelous phosphate, $P_2O_2Nio''_3$, is formed as a pale-green hydrated precipitate when hydric disodic phosphate is added to the solution of a nickel salt. On heating, it becomes anhydrous and turns yellow.

Nickelous arsenate, $As_2O_2Nio''_3,8OH_2$, occurs native as the mineral *nickel bloom*, in green capillary crystals or as an efflorescence.

COMPOUNDS OF NICKEL WITH SULPHUR.

NICKELOUS SULPHIDE, NiS'', occurs native as *millerite* or *capillary pyrites* in brass-yellow hexagonal and generally capillary crystals. It is formed when nickel and sulphur are heated together. Ammonic sulphide precipitates from solutions of nickel salts black hydrated

amorphous nickelous sulphide, and if yellow ammonic sulphide has been employed, an excess of this precipitant dissolves a portion of the precipitate, yielding a brown solution. The precipitate is slowly oxidized by exposure to the air when moist. The precipitated compound dissolves with difficulty in hydrochloric acid; and this acid is totally without action upon the native sulphide or upon that prepared in the dry way.

Nickelic disulphide, NiS''_2, is obtained by fusing a mixture of nickelous carbonate and sodic carbonate with an excess of sulphur. On extracting the mass with water the disulphide remains as a dark iron-gray impalpable powder.

General Properties and Reactions of the Compounds of Nickel.—The aquates of the salts of nickel are of an apple-green color; the anhydrous salts are yellow. *Caustic alkalies* precipitate pale-green nickelous hydrate, which is not altered either by boiling or by exposure to air. *Ammonia* gives a similar precipitate, soluble in excess, yielding a greenish-blue liquid; in presence of salts of ammonia no precipitate is formed. *Sulphuretted hydrogen* produces no precipitate in solutions with strong acids; *ammonic sulphide* precipitates black hydrated nickelous sulphide, slightly soluble in excess, yielding a brown solution. The sulphide is scarcely soluble in dilute hydrochloric acid, readily soluble in aqua-regia. *Potassic ferrocyanide* precipitates greenish-white nickelous ferrocyanide ($Ni''_2Fe''Cy_6$); *potassic ferricyanide* precipitates yellowish-brown nickelous ferricyanide ($Ni''_3{}'Fe'''_2Cy_{12}$). *Potassic cyanide* produces a yellowish-green precipitate of nickelous cyanide, soluble in excess of the precipitant with formation of a double salt. From this solution acids reprecipitate nickelous cyanide, and if the solution be warmed with sodic hypochlorite the nickel is precipitated as black hydrated nickelic oxide. (Cobalt is not precipitated under these circumstances by sodic hypochlorite). The compounds of nickel, when heated with sodic carbonate on charcoal in the reducing flame, yield white shining magnetic particles of metallic nickel. With borax and microcosmic salt the compounds of nickel yield characteristically colored fluxes. In the oxidizing flame the borax bead is violet while hot, reddish-brown when cold; the microcosmic salt bead is red or reddish-brown while hot, yellow, or reddish-yellow when cold. In the reducing flame the microcosmic salt bead undergoes no change, whilst the borax bead turns gray and clouded, owing to the separation of metallic nickel. The nickel compounds do not color flame.

NORWEGIUM, Ng.

Atomic weight = 214? *Sp. gr.* 9.441. *Fuses at* 254° C. (489° F.).

This rare metal has been recently discovered by Dahll in a specimen of Norwegian nickel glance. Very little is yet known concerning it. In most of its properties it closely resembles bismuth, but differs from this element in the solubility of its oxide in an excess of potassic hydrate, or of alkaline carbonates, on boiling. Assuming the correctness of the above atomic weight, the oxide possesses the formula Ng_2O_3. Excess of water decomposes its salts with precipitation of basic compounds.

INDEX.

**** In order that names of compounds may as far as possible appear under the headings of their respective elements, the numerical prefixes di, tri, etc., have been omitted in the Index, except in cases where they serve to distinguish compounds that might otherwise be confounded.*

CHOLERA, by ALFRED STILLÉ, M. D., LL. D., see inside—page 16.

LEA BROTHERS & CO.'S

(*Late HENRY C. LEA'S SON & CO.*)

CLASSIFIED CATALOGUE

OF

MEDICAL AND SURGICAL

PUBLICATIONS.

In asking the attention of the profession to the works advertised in the following pages, the publishers would state that no pains are spared to secure a continuance of the confidence earned for the publications of the house by their careful selection and accuracy and finish of execution.

The large number of inquiries received from the profession for a finer class of bindings than is usually placed on medical books has induced us to put certain of our standard publications in half Russia; and, that the growing taste may be encouraged, the prices have been fixed at so small an advance over the cost of sheep as to place it within the means of all to possess a library that shall have attractions as well for the eye as for the mind of the reading practitioner.

The printed prices are those at which books can generally be supplied by booksellers throughout the United States, who can readily procure for their customers any works not kept in stock. Where access to bookstores is not convenient, books will be sent by mail postpaid on receipt of the price, and as the limit of mailable weight has been removed, no difficulty will be experienced in obtaining through the post-office any work in this catalogue. No risks, however, are assumed either on the money or on the books, and no publications but our own are supplied, so that gentlemen will in most cases find it more convenient to deal with the nearest bookseller.

LEA BROTHERS & CO.

Nos. 706 and 708 Sansom St., Philadelphia, September, 1885.

PROSPECTUS FOR 1885.

A WEEKLY MEDICAL JOURNAL.

SUBSCRIPTION RATES.

The Medical News	Five Dollars.
The American Journal of the Medical Sciences .	Five Dollars.

COMMUTATION RATES.

The Medical News The American Journal of the Medical Sciences	Nine Dollars per annum, in advance.

THE MEDICAL NEWS.

A National Weekly Medical Periodical, containing 28 to 32 Quarto Pages of Reading Matter in Each Issue.

The Medical News endeavors to render efficient assistance in the daily work of the practising physician, surgeon and specialist. Every department of medical science finds adequate representation in its columns, and its plan and arrangement are well calculated to suit the convenience and secure the comfort of its readers. In the

THE MEDICAL NEWS—WEEKLY.

(Continued from first page.)

Original Department its columns are replete with articles of the highest practical value; its Hospital Reports reflect the modes of treatment adopted in the most celebrated hospitals of the globe, and its Department of Progress contains judicious excerpts and translations from all the leading medical periodicals of the world. The Editorial Articles are from the pens of a large and able Editorial Staff, and are everywhere conceded to be the most instructive and scholarly productions of their class in the country. Maintaining a large corps of qualified correspondents in all the medical centres of both hemispheres, THE NEWS is in early receipt, by cable, telegraph and mail, of intelligence from all quarters. It thus unites the energy of a newspaper with the elaboration of a scientific magazine. Its reputation for enterprise in the past is the best guarantee for the future that nothing will be left undone to render it a faithful counsellor and indispensable assistant to every professional man in active practice.

THE AMERICAN JOURNAL of the MEDICAL SCIENCES,

Edited by I. MINIS HAYS, A. M., M. D.,

Is published Quarterly, on the first days of January, April, July and October, each Number containing over Three Hundred Octavo Pages, fully Illustrated.

In his contribution to "A Century of American Medicine," published in 1876, Dr. John S. Billings, U. S. A., Librarian of the National Medical Library, Washington, thus graphically outlines the character and services of THE AMERICAN JOURNAL—"The ninety-seven volumes of this Journal need no eulogy. They contain many original papers of the highest value; nearly all the real criticisms and reviews which we possess; and such carefully prepared summaries of the progress of medical science, and abstracts and notices of foreign works, that from this file alone, were all other productions of the press for the last fifty years destroyed, it would be possible to reproduce the great majority of the real contributions of the world to medical science during that period."

This opinion of a man pre-eminently qualified to judge is corroborated by the great circle of readers of the Journal, which includes the thinkers of the profession in all parts of the world. During the coming year the features of the Journal which have given unalloyed satisfaction to two generations of medical men, will be maintained in their vigorous maturity.

The **Original Department** will consist of elaborate and richly illustrated articles from the pens of the most eminent members of the profession in all parts of the country and England.

The **Review Department** will maintain its well-earned reputation for discernment and impartiality, and will contain elaborate reviews of new works and topics of the day, and numerous analytical and bibliographical notices by competent writers.

Following these comes the **Quarterly Summary of Improvements and Discoveries in the Medical Sciences**, which, being a classified and arranged condensation of important articles appearing in the chief medical journals of the world, furnishes a compact digest of medical progress abroad and at home.

The subscription price of THE AMERICAN JOURNAL OF THE MEDICAL SCIENCES has never been raised during its long career. It is still sent free of postage for Five Dollars per annum in advance.

Taken together, the JOURNAL and NEWS combine the advantages of the elaborate preparation that can be devoted to a quarterly with the prompt conveyance of intelligence by the weekly; while, by special management, duplication of matter is rendered impossible.

It will thus be seen that for the very moderate sum of NINE DOLLARS in advance the subscriber will receive free of postage a weekly and a quarterly journal, both reflecting the latest advances of the medical sciences, and containing an equivalent of more than 4000 octavo pages, stored with the choicest material, original and selected, that can be furnished by the best medical minds of both hemispheres. It would be impossible to find elsewhere so large an amount of matter of the same value offered at so low a price.

☞ The safest mode of remittance is by bank check or postal money order, drawn to the order of the undersigned; where these are not accessible, remittances for subscriptions may be made at the risk of the publishers by forwarding in *registered* letters. Address,

LEA BROTHERS & CO., Nos. 706 and 708 Sansom St., Philadelphia.

*** Communications to both these periodicals are invited from gentlemen in all parts of the country. Original articles contributed exclusively to either periodical are liberally paid for upon publication. When necessary to elucidate the text, illustrations will be furnished without cost to the author.

All letters pertaining to the *Editorial Department* of THE MEDICAL NEWS and THE AMERICAN JOURNAL OF THE MEDICAL SCIENCES should be addressed to the EDITORIAL OFFICES, 1004 Walnut Street, Philadelphia.

All letters pertaining to the *Business Department* of these journals should be addressed *exclusively* to LEA BROTHERS & CO., 706 and 708 Sansom Street, Philadelphia.

HARTSHORNE, HENRY, A. M., M. D., LL. D.,

Lately Professor of Hygiene in the University of Pennsylvania.

A Conspectus of the Medical Sciences; Containing Handbooks on Anatomy, Physiology, Chemistry, Materia Medica, Practice of Medicine, Surgery and Obstetrics. Second edition, thoroughly revised and greatly improved. In one large royal 12mo. volume of 1028 pages, with 477 illustrations. Cloth, $4.25; leather, $5.00.

The object of this manual is to afford a convenient work of reference to students during the brief moments at their command while in attendance upon medical lectures. It is a favorable sign that it has been found necessary, in a short space of time, to issue a new and carefully revised edition. The illustrations are very numerous and unusually clear, and each part seems to have received its due share of attention. We can conceive such a work to be useful, not only to students, but to practitioners as well. It reflects credit upon the industry and energy of its able editor.—*Boston Medical and Surgical Journal*, Sept. 3, 1874.

We can say, with the strictest truth, that it is the best work of the kind with which we are acquainted. It embodies in a condensed form all recent contributions to practical medicine, and is therefore useful to every busy practitioner throughout our country, besides being admirably adapted to the use of students of medicine. The book is faithfully and ably executed.—*Charleston Medical Journal*, April, 1875.

STUDENTS' SERIES OF MANUALS.

A Series of Fifteen Manuals, for the use of Students and Practitioners of Medicine and Surgery, written by eminent Teachers or Examiners, and issued in pocket-size 12mo. volumes of 300-540 pages, richly illustrated and at a low price. The following volumes are now ready: BELL'S *Comparative Physiology and Anatomy*, GOULD'S *Surgical Diagnosis*, ROBERTSON'S *Physiological Physics*, BRUCE'S *Materia Medica and Therapeutics*, POWER'S *Human Physiology*, CLARKE and LOCKWOOD'S *Dissectors' Manual*, RALFE'S *Clinical Chemistry*, TREVES' *Surgical Applied Anatomy*, PEPPER'S *Surgical Pathology*, and KLEIN'S *Elements of Histology*. The following are in press: BELLAMY'S *Operative Surgery*, PEPPER'S *Forensic Medicine, and* CURNOW'S *Medical Applied Anatomy*. For separate notices see index on last page.

SERIES OF CLINICAL MANUALS.

In arranging for this Series it has been the design of the publishers to provide the profession with a collection of authoritative monographs on important clinical subjects in a cheap and portable form. The volumes will contain about 550 pages and will be freely illustrated by chromo-lithographs and woodcuts. The following volumes are just ready: BUTLIN on the *Tongue;* TREVES on *Intestinal Obstruction;* and SAVAGE on *Insanity and Allied Neuroses;* The following are in active preparation: HUTCHINSON on *Syphilis;* BRYANT on the *Breast;* MORRIS on *Surgical Diseases of the Kidney;* BROADBENT on the *Pulse;* OWEN on *Surgical Diseases of Children;* LUCAS on *Diseases of the Urethra;* MARSH on *Diseases of the Joints*, PICK on *Fractures and Dislocations*, and BALL on the *Rectum and Anus*. For separate notices see index on last page.

NEILL, JOHN, M. D., and SMITH, F. G., M. D.,

Late Surgeon to the Penna. Hospital. — *Prof. of the Institutes of Med. in the Univ. of Penna.*

An Analytical Compendium of the Various Branches of Medical Science, for the use and examination of Students. A new edition, revised and improved. In one large royal 12mo. volume of 974 pages, with 374 woodcuts. Cloth, $4; leather, $4.75.

LUDLOW, J. L., M. D.,

Consulting Physician to the Philadelphia Hospital, etc.

A Manual of Examinations upon Anatomy, Physiology, Surgery, Practice of Medicine, Obstetrics, Materia Medica, Chemistry, Pharmacy and Therapeutics. To which is added a Medical Formulary. 3d edition, thoroughly revised, and greatly enlarged. In one 12mo. volume of 816 pages, with 370 illustrations. Cloth, $3.25; leather, $3.75.

The arrangement of this volume in the form of question and answer renders it especially suitable for the office examination of students, and for those preparing for graduation.

DUNGLISON, ROBLEY, M. D.,

Late Professor of Institutes of Medicine in the Jefferson Medical College of Philadelphia.

MEDICAL LEXICON; A Dictionary of Medical Science: Containing a concise Explanation of the various Subjects and Terms of Anatomy, Physiology, Pathology, Hygiene, Therapeutics, Pharmacology, Pharmacy, Surgery, Obstetrics, Medical Jurisprudence and Dentistry, Notices of Climate and of Mineral Waters, Formulæ for Officinal, Empirical and Dietetic Preparations, with the Accentuation and Etymology of the Terms, and the French and other Synonymes, so as to constitute a French as well as an English Medical Lexicon. Edited by RICHARD J. DUNGLISON, M. D. In one very large and handsome royal octavo volume of 1139 pages. Cloth, $6.50; leather, raised bands, $7.50; very handsome half Russia, raised bands, $8.

The object of the author, from the outset, has not been to make the work a mere lexicon or dictionary of terms, but to afford under each word a condensed view of its various medical relations, and thus to render the work an epitome of the existing condition of medical science. Starting with this view, the immense demand which has existed for the work has enabled him, in repeated revisions, to augment its completeness and usefulness, until at length it has attained the position of a recognized and standard authority wherever the language is spoken. Special pains have been taken in the preparation of the present edition to maintain this enviable reputation. The additions to the vocabulary are more numerous than in any previous revision, and particular attention has been bestowed on the accentuation, which will be found marked on every word. The typographical arrangement has been greatly improved, rendering reference much more easy, and every care has been taken with the mechanical execution. The volume now contains the matter of at least four ordinary octavos.

A book of which every American ought to be proud. When the learned author of the work passed away, probably all of us feared lest the book should not maintain its place in the advancing science whose terms it defines. Fortunately, Dr. Richard J. Dunglison, having assisted his father in the revision of several editions of the work, and having been, therefore, trained in the methods and imbued with the spirit of the book, has been able to edit it as a work of the kind should be edited—to carry it on steadily, without jar or interruption, along the grooves of thought it has travelled during its lifetime. To show the magnitude of the task which Dr. Dunglison has assumed and carried through, it is only necessary to state that more than six thousand new subjects have been added in the present edition.—*Philadelphia Medical Times*, Jan. 3, 1874.

About the first book purchased by the medical student is the Medical Dictionary. The lexicon explanatory of technical terms is simply a *sine qua non*. In a science so extensive and with such collaterals as medicine, it is as much a necessity also to the practising physician. To meet the wants of students and most physicians the dictionary must be condensed while comprehensive, and practical while perspicacious. It was because Dunglison's met these indications that it became at once the dictionary of general use wherever medicine was studied in the English language. In no former revision have the alterations and additions been so great. The chief terms have been set in black letter, while the derivatives follow in small caps; an arrangement which greatly facilitates reference. —*Cincinnati Lancet and Clinic*, Jan. 10, 1874.

As a standard work of reference Dunglison's work has been well known for about forty years, and needs no words of praise on our part to recommend it to the members of the medical, and likewise of the pharmaceutical, profession. The latter especially are in need of a work which gives ready and reliable information on thousands of subjects and terms which they are liable to encounter in pursuing their daily vocations, but with which they cannot be expected to be familiar. The work before us fully supplies this want.—*American Journal of Pharmacy*, Feb. 1874.

Particular care has been devoted to derivation and accentuation of terms. With regard to the latter, indeed, the present edition may be considered a complete "Pronouncing Dictionary of Medical Science." It is perhaps the most reliable work published for the busy practitioner, as it contains information upon every medical subject, in a form for ready access, and with a brevity as admirable as it is practical.—*Southern Medical Record*, Feb. 1874.

A valuable dictionary of the terms employed in medicine and the allied sciences, and of the relations of the subjects treated under each head. It well deserves the authority and popularity it has obtained.—*British Med. Jour.*, Oct. 31, 1874.

Few works of this class exhibit a grander monument of patient research and of scientific lore.—*London Lancet*, May 13, 1875.

Dunglison's Dictionary is incalculably valuable, and indispensable to every practitioner of medicine, pharmacist and dentist.—*Western Lancet*, March, 1874.

It has the rare merit that it certainly has no rival in the English language for accuracy and extent of references.—*London Medical Gazette.*

HOBLYN, RICHARD D., M. D.

A Dictionary of the Terms Used in Medicine and the Collateral Sciences. Revised, with numerous additions, by ISAAC HAYS, M. D., late editor of The American Journal of the Medical Sciences. In one large royal 12mo. volume of 520 double-columned pages. Cloth, $1.50; leather, $2.00.

It is the best book of definitions we have, and ought always to be upon the student's table —*Southern Medical and Surgical Journal.*

RODWELL, G. F., F. R. A. S., F. C. S.,

Lecturer on Natural Science at Clifton College, England.

A Dictionary of Science: Comprising Astronomy, Chemistry, Dynamics, Electricity, Heat, Hydrodynamics, Hydrostatics, Light, Magnetism, Mechanics, Meteorology, Pneumatics, Sound and Statics. Contributed by J. T. Bottomley, M. A., F. C. S., William Crookes, F.R.S., F.C.S., Frederick Guthrie, B.A., Ph. D., R. A. Proctor, B.A., F.R.A.S., G. F. Rodwell, Editor, Charles Tomlinson, F.R.S., F.C.S., and Richard Wornell, M.A., B.Sc. Preceded by an Essay on the History of the Physical Sciences. In one handsome octavo volume of 702 pages, with 143 illustrations. Cloth, $5.00.

GRAY, HENRY, F. R. S.,

Lecturer on Anatomy at St. George's Hospital, London.

Anatomy, Descriptive and Surgical. The Drawings by H. V. CARTER, M. D., and Dr. WESTMACOTT. The dissections jointly by the AUTHOR and Dr. CARTER. With an Introduction on General Anatomy and Development by T. HOLMES, M. A., Surgeon to St. George's Hospital. Edited by T. Pickering Pick, F. R. C. S., Surgeon to and Lecturer on Anatomy at St. George's Hospital, London, Examiner in Anatomy, Royal College of Surgeons of England. A new American from the tenth enlarged and improved London edition. To which is added the second American from the latest English edition of LANDMARKS, MEDICAL AND SURGICAL, by LUTHER HOLDEN, F. R. C. S., author of "Human Osteology," "A Manual of Dissections," etc. In one imperial octavo volume of 1023 pages, with 564 large and elaborate engravings on wood. Cloth, $6.00; leather, $7.00; very handsome half Russia, raised bands, $7.50.

This work covers a more extended range of subjects than is customary in the ordinary text-books, giving not only the details necessary for the student, but also the application to those details to the practice of medicine and surgery. It thus forms both a guide for the learner and an admirable work of reference for the active practitioner. The engravings form a special feature in the work, many of them being the size of nature, nearly all original, and having the names of the various parts printed on the body of the cut, in place of figures of reference with descriptions at the foot. They thus form a complete and splendid series, which will greatly assist the student in forming a clear idea of Anatomy, and will also serve to refresh the memory of those who may find in the exigencies of practice the necessity of recalling the details of the dissecting-room. Combining, as it does, a complete Atlas of Anatomy with a thorough treatise on systematic, descriptive and applied Anatomy, the work will be found of great service to all physicians who receive students in their offices, relieving both preceptor and pupil of much labor in laying the groundwork of a thorough medical education.

Landmarks, Medical and Surgical, by the distinguished Anatomist, Mr. Luther Holden, has been appended to the present edition as it was to the previous one. This work gives in a clear, condensed and systematic way all the information by which the practitioner can determine from the external surface of the body the position of internal parts. Thus complete, the work, it is believed, will furnish all the assistance that can be rendered by type and illustration in anatomical study.

This well-known work comes to us as the latest American from the tenth English edition. As its title indicates, it has passed through many hands and has received many additions and revisions. The work is not susceptible of more improvement. Taking it all in all, its size, manner of make-up, its character and illustrations, its general accuracy of description, its practical aim, and its perspicuity of style, it is the Anatomy best adapted to the wants of the student and practitioner.—*Medical Record, Sept.* 15, 1883.

There is probably no work used so universally by physicians and medical students as this one. It is deserving of the confidence that they repose in it. If the present edition is compared with that issued two years ago, one will readily see how much it has been improved in that time. Many pages have been added to the text, especially in those parts that treat of histology, and many new cuts have been introduced and old ones modified. —*Journal of the American Medical Association*, Sept. 1, 1883.

ALSO FOR SALE SEPARATE—

HOLDEN, LUTHER, F. R. C. S.,

Surgeon to St. Bartholomew's and the Foundling Hospitals, London.

Landmarks, Medical and Surgical. Second American from the latest revised English edition, with additions by W. W. KEEN, M. D., Professor of Artistic Anatomy in the Pennsylvania Academy of the Fine Arts, formerly Lecturer on Anatomy in the Philadelphia School of Anatomy. In one handsome 12mo. volume of 148 pages. Cloth, $1.00.

This little book is all that can be desired within its scope, and its contents will be found simply invaluable to the young surgeon or physician, since they bring before him such data as he requires at every examination of a patient. It is written in language so clear and concise that one ought almost to learn it by heart. It teaches diagnosis by external examination, ocular and palpable, of the body, with such anatomical and physiological facts as directly bear on the subject. It is eminently the student's and young practitioner's book.—*Physician and Surgeon*, Nov. 1881.

WILSON, ERASMUS, F. R. S.

A System of Human Anatomy, General and Special. Edited by W. H. GOBRECHT, M. D., Professor of General and Surgical Anatomy in the Medical College of Ohio. In one large and handsome octavo volume of 616 pages, with 397 illustrations. Cloth, $4.00; leather, $5.00.

SMITH, H. H., M. D., and HORNER, WM. E., M. D.,

Emeritus Prof. of Surgery in the Univ. of Penna., etc. *Late Prof. of Anat. in the Univ. of Penna.*

An Anatomical Atlas, Illustrative of the Structure of the Human Body. In one large imperial octavo volume of 200 pages, with 634 beautiful figures. Cloth, $4.50.

CLELAND, JOHN, M. D., F. R. S.,

Professor of Anatomy and Physiology in Queen's College, Galway.

A Directory for the Dissection of the Human Body. In one 12mo. volume of 178 pages. Cloth, $1.25.

ALLEN, HARRISON, M. D.,

Professor of Physiology in the University of Pennsylvania.

A System of Human Anatomy, Including Its Medical and Surgical Relations. For the use of Practitioners and Students of Medicine. With an Introductory Section on Histology. By E. O. SHAKESPEARE, M. D., Ophthalmologist to the Philadelphia Hospital. Comprising 813 double-columned quarto pages, with 380 illustrations on 109 full page lithographic plates, many of which are in colors, and 241 engravings in the text. In six Sections, each in a portfolio. Section I. HISTOLOGY. Section II. BONES AND JOINTS. Section III. MUSCLES AND FASCIÆ. Section IV. ARTERIES, VEINS AND LYMPHATICS. Section V. NERVOUS SYSTEM. Section VI. ORGANS OF SENSE, OF DIGESTION AND GENITO-URINARY ORGANS, EMBRYOLOGY, DEVELOPMENT, TERATOLOGY, SUPERFICIAL ANATOMY, POST-MORTEM EXAMINATIONS, AND GENERAL AND CLINICAL INDEXES. Price per Section, each in a handsome portfolio, $3.50; also bound in one volume, cloth $23.00; very handsome half Russia, raised bands and open back, $25.00. *For sale by subscription only. Apply to the Publishers.*

Extract from Introduction.

It is the design of this book to present the facts of human anatomy in the manner best suited to the requirements of the student and the practitioner of medicine. The author believes that such a book is needed, inasmuch as no treatise, as far as he knows, contains, in addition to the text descriptive of the subject, a systematic presentation of such anatomical facts as can be applied to practice.

A book which will be at once accurate in statement and concise in terms; which will be an acceptable expression of the present state of the science of anatomy; which will exclude nothing that can be made applicable to the medical art, and which will thus embrace all of surgical importance, while omitting nothing of value to clinical medicine,—would appear to have an excuse for existence in a country where most surgeons are general practitioners, and where there are few general practitioners who have no interest in surgery.

It is to be considered a study of applied anatomy in its widest sense—a systematic presentation of such anatomical facts as can be applied to the practice of medicine as well as of surgery. Our author is concise, accurate and practical in his statements, and succeeds admirably in infusing an interest into the study of what is generally considered a dry subject. The department of Histology is treated in a masterly manner, and the ground is travelled over by one thoroughly familiar with it. The illustrations are made with great care, and are simply superb. There is as much of practical application of anatomical points to the every-day wants of the medical clinician as to those of the operating surgeon. In fact, few general practitioners will read the work without a feeling of surprised gratification that so many points, concerning which they may never have thought before are so well presented for their consideration. It is a work which is destined to be the best of its kind in any language.—*Medical Record*, Nov. 25, 1882.

CLARKE, W. B., F.R.C.S. & LOCKWOOD, C. B., F.R.C.S.

Demonstrators of Anatomy at St. Bartholomew's Hospital Medical School, London.

The Dissector's Manual. In one pocket-size 12mo. volume of 396 pages, with 49 illustrations. Limp cloth, red edges, $1.50. *Just ready.* See *Students' Series of Manuals*, page 3.

This is a very excellent manual for the use of the student who desires to learn anatomy. The methods of demonstration seem to us very satisfactory. There are many woodcuts which, for the most part, are good and instructive. The book is neat and convenient. We are glad to recommend it.—*Boston Medical and Surgical Journal*, Jan. 17, 1884.

TREVES, FREDERICK, F. R. C. S.,

Senior Demonstrator of Anatomy and Assistant Surgeon at the London Hospital.

Surgical Applied Anatomy. In one pocket-size 12mo. volume of 540 pages, with 61 illustrations. Limp cloth, red edges, $2.00. *Just ready.* See *Students' Series of Manuals*, page 3.

He has produced a work which will command a larger circle of readers than the class for which it was written. This union of a thorough, practical acquaintance with these fundamental branches, quickened by daily use as a teacher and practitioner, has enabled our author to prepare a work which it would be a most difficult task to excel.—*The American Practitioner* Feb. 1884.

CURNOW, JOHN, M. D., F. R. C. P.,

Professor of Anatomy at King's College, Physician at King's College Hospital.

Medical Applied Anatomy. In one pocket-size 12mo. volume. *Preparing.* See *Students' Series of Manuals*, page 3.

BELLAMY, EDWARD, F. R. C. S.,

Senior Assistant-Surgeon to the Charing-Cross Hospital, London.

The Student's Guide to Surgical Anatomy: Being a Description of the most Important Surgical Regions of the Human Body, and intended as an Introduction to operative Surgery. In one 12mo. volume of 300 pages, with 50 illustrations. Cloth, $2.25.

HARTSHORNE'S HANDBOOK OF ANATOMY AND PHYSIOLOGY. Second edition, revised. In one royal 12mo. volume of 310 pages, with 220 woodcuts. Cloth, $1.75.

HORNER'S SPECIAL ANATOMY AND HISTOLOGY. Eighth edition, extensively revised and modified. In two octavo volumes of 1007 pages, with 320 woodcuts. Cloth, $6.00.

DRAPER, JOHN C., M. D., LL. D.,

Professor of Chemistry in the University of the City of New York.

Medical Physics. A Text-book for Students and Practitioners of Medicine. In one octavo volume of 734 pages, with 376 woodcuts, mostly original. Cloth, $4. *Just ready.*

From the Preface.

The fact that a knowledge of Physics is indispensable to a thorough understanding of Medicine has not been as fully realized in this country as in Europe, where the admirable works of Desplats and Gariel, of Robertson and of numerous German writers constitute a branch of educational literature to which we can show no parallel. A full appreciation of this the author trusts will be sufficient justification for placing in book form the substance of his lectures on this department of science, delivered during many years at the University of the City of New York.

Broadly speaking, this work aims to impart a knowledge of the relations existing between Physics and Medicine in their latest state of development, and to embody in the pursuit of this object whatever experience the author has gained during a long period of teaching this special branch of applied science.

Certainly we have no text-book as full as the excellent one he has prepared. It begins with a statement of the properties of matter and energy. After these the special departments of physics are explained, acoustics, optics, heat, electricity and magnetism, closing with a section on electro-biology. The applications of all these to physiology and medicine are kept constantly in view. The text is amply illustrated and the many difficult points of the subject are brought forward with remarkable clearness and ability.—*Medical and Surgical Reporter*, July 18, 1885. q.

The volume from beginning to end teems with useful information. Take the book as a whole and it is one of the most valuable scientific treatises given to the medical profession for a number of years. It is profusely and handsomely illustrated. The work should have a place upon every physician's library shelf.—*Maryland Medical Journal*, July 18, 1885. q.

This is the only work with which we are acquainted in which physics is treated with reference to medicine. Preceptors who are axious that their pupils should have a scientific knowledge of medicine, should make this work a text-book, and require a thorough study of it.—*Cincinnati Medical News*, July 18, 1885. q.

ROBERTSON, J. McGREGOR, M. A., M. B.,

Muirhead Demonstrator of Physiology, University of Glasgow.

Physiological Physics. In one 12mo. volume of 537 pages, with 219 illustrations. Limp cloth, $2.00. *Just ready.* See *Students' Series of Manuals*, page 3.

The title of this work sufficiently explains the nature of its contents. It is designed as a manual for the student of medicine, an auxiliary to his text-book in physiology, and it would be particularly useful as a guide to his laboratory experiments. It will be found of great value to the practitioner. It is a carefully prepared book of reference, concise and accurate, and as such we heartily recommend it.—*Journal of the American Medical Association*, Dec. 6, 1884.

DALTON, JOHN C., M. D.,

Professor Emeritus of Physiology in the College of Physicians and Surgeons, New York.

Doctrines of the Circulation of the Blood. A History of Physiological Opinion and Discovery in regard to the Circulation of the Blood. In one handsome 12mo. volume of 293 pages. Cloth, $2. *Just ready.*

Dr. Dalton's work is the fruit of the deep research of a cultured mind, and to the busy practitioner it cannot fail to be a source of instruction. It will inspire him with a feeling of gratitute and admiration for those plodding workers of olden times, who laid the foundation of the magnificent temple of medical science as it now stands.—*New Orleans Medical and Surgical Journal*, Aug. 1885.

In the progress of physiological study no fact was of greater moment, none more completely revolutionized the theories of teachers, than the discovery of the circulation of the blood. This explains the extraordinary interest it has to all medical historians. The volume before us is one of three or four which have been written within a few years by American physicians. It is in several respects the most complete. The volume, though small in size, is one of the most creditable contributions from an American pen to medical history that has appeared.—*Med. & Surg. Rep.*, Dec. 6, 1884.

BY THE SAME AUTHOR.

The Topographical Anatomy of the Brain. In three very handsome quarto volumes comprising 178 pages of descriptive text. Illustrated with 48 full page photographic plates of Brain Sections, with a like number of explanatory plates, as well as many woodcuts through the text.

BELL, F. JEFFREY, M. A.,

Professor of Comparative Anatomy at King's College, London.

Comparative Physiology and Anatomy. In one 12mo. volume of 561 pages, with 229 illustrations. Limp cloth, $2.00. *Just ready.* See *Students' Series of Manuals*, page 3.

ELLIS, GEORGE VINER,

Emeritus Professor of Anatomy in University College, London.

Demonstrations of Anatomy. Being a Guide to the Knowledge of the Human Body by Dissection. From the eighth and revised London edition. In one very handsome octavo volume of 716 pages, with 249 illustrations. Cloth, $4.25; leather, $5.25.

ROBERTS, JOHN B., A. M., M. D.,

Prof. of Applied Anat. and Oper. Surg. in Phila. Polyclinic and Coll. for Graduates in Medicine.

The Compend of Anatomy. For use in the dissecting-room and in preparing for examinations. In one 16mo. volume of 196 pages. Limp cloth, 75 cents.

DALTON, JOHN C., M. D.,

Professor of Physiology in the College of Physicians and Surgeons, New York, etc.

A Treatise on Human Physiology. Designed for the use of Students and Practitioners of Medicine. Seventh edition, thoroughly revised and rewritten. In one very handsome octavo volume of 722 pages, with 252 beautiful engravings on wood. Cloth, $5.00; leather, $6.00; very handsome half Russia, raised bands, $6.50.

The merits of Professor Dalton's text-book, his smooth and pleasing style, the remarkable clearness of his descriptions, which leave not a chapter obscure, his cautious judgment and the general correctness of his facts, are perfectly known. They have made his text-book the one most familiar to American students.—*Med. Record*, March 4, 1882.

Certainly no physiological work has ever issued from the press that presented its subject-matter in a clearer and more attractive light. Almost every page bears evidence of the exhaustive revision that has taken place. The material is placed in a more compact form, yet its delightful charm is retained, and no subject is thrown into obscurity. Altogether this edition is far in advance of any previous one, and will tend to keep the profession posted as to the most recent additions to our physiological knowledge.—*Michigan Medical News*, April, 1882.

One can scarcely open a college catalogue that does not have mention of Dalton's *Physiology* as the recommended text or consultation-book. For American students we would unreservedly recommend Dr. Dalton's work.—*Va. Med. Monthly*, July,'82.

FOSTER, MICHAEL, M. D., F. R. S.,

Prelector in Physiology and Fellow of Trinity College, Cambridge, England.

Text-Book of Physiology. Third American from the fourth English edition, with notes and additions by E. T. REICHERT, M. D. In one handsome royal 12mo. volume of 908 pages, with 271 illustrations. Cloth, $3.25; leather, $3.75. *Just ready.*

Dr. Foster's work upon physiology is so well-known as a text-book in this country, that it needs but little to be said in regard to it. There is scarcely a medical college in the United States where it is not in the hands of the students. The author, more than any other writer with whom we are acquainted, seems to understand what portions of the science are essential for students to know and what may be passed over by them as not important. From the beginning to the end, physiology is taught in a systematic manner. To this third American edition numerous additions, corrections and alterations have been made, so that in its present form the usefulness of the book will be found to be much increased.—*Cincinnati Medical News*, July 1885.

POWER, HENRY, M. B., F. R. C. S.,

Examiner in Physiology, Royal College of Surgeons of England.

Human Physiology. In one handsome pocket-size 12mo. volume of 396 pages, with 47 illustrations. Cloth, $1.50. See *Students' Series of Manuals*, page 3.

The prominent character of this work is that of judicious condensation, in which an able and successful effort appears to have been made by its accomplished author to teach the greatest number of facts in the fewest possible words. The result is a specimen of concentrated intellectual pabulum seldom surpassed, which ought to be carefully ingested and digested by every practitioner who desires to keep himself well informed upon this most progressive of the medical sciences. The volume is one which we cordially recommend to every one of our readers.—*The American Journal of the Medical Sciences*, October, 1884.

This little work is deserving of the highest praise, and we can hardly conceive how the main facts of this science could have been more clearly or concisely stated. The price of the work is such as to place it within the reach of all, while the excellence of its text will certainly secure for it most favorable commendation.—*Cincinnati Lancet and Clinic*, Feb. 16, 1884.

CARPENTER, WM. B., M. D., F. R. S., F. G. S., F. L. S.,

Registrar to the University of London, etc.

Principles of Human Physiology. Edited by HENRY POWER, M. B., Lond., F. R. C. S., Examiner in Natural Sciences, University of Oxford. A new American from the eighth revised and enlarged edition, with notes and additions by FRANCIS G. SMITH, M. D., late Professor of the Institutes of Medicine in the University of Pennsylvania. In one very large and handsome octavo volume of 1083 pages, with two plates and 373 illustrations. Cloth, $5.50; leather, $6.50; half Russia, $7.

FOWNES, GEORGE, Ph. D.

A Manual of Elementary Chemistry; Theoretical and Practical. Embodying WATTS' *Inorganic Chemistry.* New American edition. In one large royal 12mo. volume of over 1000 pages, with 200 illustrations on wood and a colored plate. Cloth, $2.75; leather, $3.25. *In a few days.*

A notice of the previous edition is appended.

The book opens with a treatise on Chemical Physics, including Heat, Light, Magnetism and Electricity. These subjects are treated clearly and briefly, but enough is given to enable the student to comprehend the facts and laws of Chemistry proper. It is the fashion of late years to omit these topics from works on chemistry but their omission is not to be commended. As was required by the great advance in the science of Chemistry of late years, the chapter on the General Principles of Chemical Philosophy has been entirely rewritten. The latest views on Equivalents, Quantivalence, etc., are clearly and fully set forth. This last edition is a great improvement upon its predecessors, which is saying not a little of a book that has reached its twelfth edition.—*Ohio Medical Recorder*, Oct., 1878.

Wöhler's Outlines of Organic Chemistry. Edited by FITTIG. Translated by IRA REMSEN, M. D., Ph. D. In one 12mo. volume of 550 pages. Cloth, $3.

GALLOWAY'S QUALITATIVE ANALYSIS. New edition.

LEHMANN'S MANUAL OF CHEMICAL PHYSIOLOGY. In one octavo volume of 327 pages, with 41 illustrations. Cloth, $2.25.

CARPENTER'S PRIZE ESSAY ON THE USE AND ABUSE OF ALCOHOLIC LIQUORS IN HEALTH AND DISEASE. With explanations of scientific words. Small 12mo. 178 pages. Cloth, 60 cents.

FRANKLAND, E., D. C. L., F. R. S., & JAPP, F. R., F. I. C.,

Professor of Chemistry in the Normal School of Science, London. *Assist. Prof. of Chemistry in the Normal School of Science, London.*

Inorganic Chemistry. In one handsome octavo volume of 600 pages, with 51 woodcuts and 2 lithographic plates. Cloth, $3.75; leather, $4.75. *In a few days.*

This work on elementary chemistry is based upon principles of classification, nomenclature and notation which have been proved by nearly twenty years experience in teaching to impart most readily a sound and accurate knowledge of the science.

ATTFIELD, JOHN, Ph. D.,

Professor of Practical Chemistry to the Pharmaceutical Society of Great Britain, etc.

Chemistry, General, Medical and Pharmaceutical; Including the Chemistry of the U. S. Pharmacopœia. A Manual of the General Principles of the Science, and their Application to Medicine and Pharmacy. A new American, from the tenth English edition, specially revised by the Author. In one handsome royal 12mo. volume of 728 pages, with 87 illustrations. Cloth, $2.50; leather, $3.00.

A text-book which passes through ten editions in sixteen years must have good qualities. This remark is certainly applicable to Attfield's Chemistry, a book which is so well known that it is hardly necessary to do more than note the appearance of this new and improved edition. It seems, however, desirable to point out that feature of the book which, in all probability, has made it so popular. There can be little doubt that it is its thoroughly practical character, the expression being used in its best sense. The author understands what the student ought to learn, and is able to put himself in the student's place and to appreciate his state of mind.—*American Chemical Journal*, April, 1884.

It is a book on which too much praise cannot be bestowed. As a text-book for medical schools it is unsurpassable in the present state of chemical science, and having been prepared with a special view towards medicine and pharmacy, it is alike indispensable to all persons engaged in those departments of science. It includes the whole chemistry of the last Pharmacopœia.—*Pacific Medical and Sugrical Journal*, Jan. 1884.

BLOXAM, CHARLES L.,

Professor of Chemistry in King's College, London.

Chemistry, Inorganic and Organic. New American from the fifth London edition, thoroughly revised and much improved. In one very handsome octavo volume of 727 pages, with 292 illustrations. Cloth, $3.75; leather, $4.75.

Comment from us on this standard work is almost superfluous. It differs widely in scope and aim from that of Attfield, and in its way is equally beyond criticism. It adopts the most direct methods in stating the principles, hypotheses and facts of the science. Its language is so terse and lucid, and its arrangement of matter so logical in sequence that the student never has occasion to complain that chemistry is a hard study. Much attention is paid to experimental illustrations of chemical principles and phenomena, and the mode of conducting these experiments. The book maintains the position it has always held as one of the best manuals of general chemistry in the English language.—*Detroit Lancet*, Feb. 1884.

The general plan of this work remains the same as in previous editions, the evident object being to give clear and concise descriptions of all known elements and of their most important compounds, with explanations of the chemical laws and principles involved. We gladly repeat now the opinion we expressed about a former edition, that we regard Bloxam's Chemistry as one of the best treatises on general and applied chemistry.—*American Jour. of Pharmacy*, Dec. 1883.

SIMON, W., Ph. D., M. D.,

Professor of Chemistry and Toxicology in the College of Physicians and Surgeons, Baltimore, and Professor of Chemistry in the Maryland College of Pharmacy.

Manual of Chemistry. A Guide to Lectures and Laboratory work for Beginners in Chemistry. A Text-book, specially adapted for Students of Pharmacy and Medicine. In one 8vo. vol. of 410 pp., with 16 woodcuts and 7 plates, mostly of actual deposits, with colors illustrating 56 of the most important chemical reactions. Cloth, $3.00; also without plates, cloth, $2.50. *Just ready.*

This book supplies a want long felt by students of medicine and pharmacy, and is a concise but thorough treatise on the subject. The long experience of the author as a teacher in schools of medicine and pharmacy is conspicuous in the perfect adaptation of the work to the special needs of the student of these branches. The colored plates, beautifully executed, illustrating precipitates of various reactions, form a novel and valuable feature of the book, and cannot fail to be appreciated by both student and teacher as a help over the hard places of the science.—*Maryland Medical Journal*, Nov. 22, 1884.

REMSEN, IRA, M. D., Ph. D.,

Professor of Chemistry in the Johns Hopkins University, Baltimore.

Principles of Theoretical Chemistry, with special reference to the Constitution of Chemical Compounds. Second and revised edition. In one handsome royal 12mo. volume of 240 pages. Cloth, $1.75. *Just ready.*

The book is a valuable contribution to the chemical literature of instruction. That in so few years a second edition has been called for indicates that many chemical teachers have been found ready to endorse its plan and to adopt its methods. In this edition a considerable proportion of the book has been rewritten, much new matter has been added and the whole has been brought up to date. We earnestly commend this book to every student of chemistry. The high reputation of the author assures its accuracy in all matters of fact, and its judicious conservatism in matters of theory, combined with the fulness with which, in a small compass, the present attitude of chemical science towards the constitution of compounds is considered, gives it a value much beyond that accorded to the average text-books of the day.—*American Journal of Science*, March, 1884.

CHARLES, T. CRANSTOUN, M. D., F. C. S., M. S.,

Formerly Asst. Prof. and Demonst. of Chemistry and Chemical Physics, Queen's College, Belfast.

The Elements of Physiological and Pathological Chemistry. A Handbook for Medical Students and Practitioners. Containing a general account of Nutrition, Foods and Digestion, and the Chemistry of the Tissues, Organs, Secretions and Excretions of the Body in Health and in Disease. Together with the methods for preparing or separating their chief constituents, as also for their examination in detail, and an outline syllabus of a practical course of instruction for students. In one handsome octavo volume of 463 pages, with 38 woodcuts and 1 colored plate. Cloth, $3.50.

The work is thoroughly trustworthy, and informed throughout by a genuine scientific spirit. The author deals with the chemistry of the digestive secretions in a systematic manner, which leaves nothing to be desired, and in reality supplies a want in English literature. The book appears to us to be at once full and systematic, and to show a just appreciation of the relative importance of the various subjects dealt with.—*British Medical Journal*, November 29, 1884.

Dr. Charles' manual admirably fulfils its intention of giving his readers on the one hand a summary, comprehensive but remarkably compact, of the mass of facts in the sciences which have become indispensable to the physician; and, on the other hand, of a system of practical directions so minute that analyses often considered formidable may be pursued by any intelligent person.—*Archives of Medicine*, Dec. 1884.

HOFFMANN, F., A.M., Ph.D., & POWER F.B., Ph.D.,

Public Analyst to the State of New York. *Prof. of Anal. Chem. in the Phil. Coll. of Pharmacy.*

A Manual of Chemical Analysis, as applied to the Examination of Medicinal Chemicals and their Preparations. Being a Guide for the Determination of their Identity and Quality, and for the Detection of Impurities and Adulterations. For the use of Pharmacists, Physicians, Druggists and Manufacturing Chemists, and Pharmaceutical and Medical Students. Third edition, entirely rewritten and much enlarged. In one very handsome octavo volume of 621 pages, with 179 illustrations. Cloth, $4.25.

We congratulate the author on the appearance of the third edition of this work, published for the first time in this country also. It is admirable and the information it undertakes to supply is both extensive and trustworthy. The selection of processes for determining the purity of the substances of which it treats is excellent and the description of them singularly explicit. Moreover, it is exceptionally free from typographical errors. We have no hesitation in recommending it to those who are engaged either in the manufacture or the testing of medicinal chemicals.—*London Pharmaceutical Journal and Transactions*, 1883.

CLOWES, FRANK, D. Sc., London,

Senior Science-Master at the High School, Newcastle-under-Lyme, etc.

An Elementary Treatise on Practical Chemistry and Qualitative Inorganic Analysis. Specially adapted for use in the Laboratories of Schools and Colleges and by Beginners. Third American from the fourth and revised English edition. In one very handsome royal 12mo. volume of about 400 pages, with about 50 illustrations. Cloth, $2.50. *In a few days.*

The style is clear, the language terse and vigorous. Beginning with a list of apparatus necessary for chemical work, he gradually unfolds the subject from its simpler to its more complex divisions. It is the most readable book of the kind we have yet seen, and is without doubt a systematic, intelligible and fully equipped laboratory guide and text book.—*Medical Record*, July 18, 1885.

We may simply repeat the favorable opinion which we expressed after the examination of the previous edition of this work. It is practical in its aims, and accurate and concise in its statements. —*American Journal of Pharmacy*, August, 1885.

RALFE, CHARLES H., M. D., F. R. C. P.,

Assistant Physician at the London Hospital.

Clinical Chemistry. In one pocket-size 12mo. volume of 314 pages, with 16 illustrations. Limp cloth, red edges, $1.50. See *Students' Series of Manuals*, page 3.

This is one of the most instructive little works that we have met with in a long time. The author is a physician and physiologist, as well as a chemist, consequently the book is unqualifiedly practical, telling the physician just what he ought to know, of the applications of chemistry in medicine. Dr. Ralfe is thoroughly acquainted with the latest contributions to his science, and it is quite refreshing to find the subject dealt with so clearly and simply, yet in such evident harmony with the modern scientific methods and spirit.—*Medical Record*, February 2, 1884.

CLASSEN, ALEXANDER,

Professor in the Royal Polytechnic School, Aix-la-Chapelle.

Elementary Quantitative Analysis. Translated, with notes and additions, by EDGAR F. SMITH, Ph. D., Assistant Professor of Chemistry in the Towne Scientific School, University of Penna. In one 12mo. volume of 324 pages, with 36 illust. Cloth, $2.00.

It is probably the best manual of an elementary nature extant insomuch as its methods are the best. It teaches by examples, commencing with single determinations, followed by separations, and then advancing to the analysis of minerals and such products as are met with in applied chemistry. It is an indispensable book for students in chemistry.—*Boston Journal of Chemistry*, Oct. 1878.

GREENE, WILLIAM H., M. D.,

Demonstrator of Chemistry in the Medical Department of the University of Pennsylvania.

A Manual of Medical Chemistry. For the use of Students. Based upon Bowman's Medical Chemistry. In one 12mo. volume of 310 pages, with 74 illus. Cloth, $1.75.

It is a concise manual of three hundred pages, giving an excellent summary of the best methods of analyzing the liquids and solids of the body, both for the estimation of their normal constituents and the recognition of compounds due to pathological conditions. The detection of poisons is treated with sufficient fulness for the purpose of the student or practitioner.—*Boston Jl. of Chem.*, June, '80.

BRUNTON, T. LAUDER, M.D., D.Sc., F.R.S., F.R.C.P.,

Lecturer on Materia Medica and Therapeutics at St. Bartholomew's Hospital, London, etc.

A Text-book of Pharmacology, Therapeutics and Materia Medica; Including the Pharmacy, the Physiological Action and the Therapeutical Uses of Drugs. In one handsome octavo volume of about 1000 pages, with 188 illustrations. Cloth, $5.50; leather, $6.50. *In press.*

It is with peculiar pleasure that the early appearance of this long expected work is announced by the publishers. Written by the foremost authority on its subject in England, it forms a compendious treatise on materia medica, pharmacology, pharmacy, and the practical use of medicines in the treatment of disease. Space has been devoted to the fundamental sciences of chemistry, physiology and pathology, wherever it seemed necessary to elucidate the proper subject-matter of the book. A general index, an index of diseases and remedies, and an index of bibliography close a volume which will undoubtedly be of the highest value to the student, practitioner and pharmacist.

It is a scientific treatise worthy to be ranked with the highest productions in physiology, either in our own or any other language. Everything is practical, the dry, hard facts of physiology being pressed into service and applied to the treatment of the commonest complaints. The information is so systematically arranged that it is available for immediate use. The index is so carefully compiled that a reference to any special point is at once obtainable. Dr. Brunton is never satisfied with vague generalities, but gives clear and precise directions for prescribing the various drugs and preparations. We congratulate students on being at last placed in possession of a scientific treatise of enormous practical importance.—*The Lancet*, June 27, 1885.

PARRISH, EDWARD,

Late Professor of the Theory and Practice of Pharmacy in the Philadelphia College of Pharmacy.

A Treatise on Pharmacy: designed as a Text-book for the Student, and as a Guide for the Physician and Pharmaceutist. With many Formulæ and Prescriptions. Fifth edition, thoroughly revised, by THOMAS S. WIEGAND, Ph. G. In one handsome octavo volume of 1093 pages, with 256 illustrations. Cloth, $5; leather, $6.

No thoroughgoing pharmacist will fail to possess himself of so useful a guide to practice, and no physician who properly estimates the value of an accurate knowledge of the remedial agents employed by him in daily practice, so far as their miscibility, compatibility and most effective methods of combination are concerned, can afford to leave this work out of the list of their works of reference. The country practitioner, who must always be in a measure his own pharmacist, will find it indispensable.—*Louisville Medical News*, March 29, 1884.

This well-known work presents itself now based upon the recently revised new Pharmacopœia. Each page bears evidence of the care bestowed upon it, and conveys valuable information from the rich store of the editor's experience. In fact, all that relates to practical pharmacy—apparatus, processes and dispensing—has been arranged and described with clearness in its various aspects, so as to afford aid and advice alike to the student and to the practical pharmacist. The work is judiciously illustrated with good woodcuts—*American Journal of Pharmacy*, January, 1884.

There is nothing to equal Parrish's *Pharmacy* in this or any other language.—*London Pharmaceutical Journal.*

HERMANN, Dr. L.,

Professor of Physiology in the University of Zurich.

Experimental Pharmacology. A Handbook of Methods for Determining the Physiological Actions of Drugs. Translated, with the Author's permission, and with extensive additions, by ROBERT MEADE SMITH, M. D., Demonstrator of Physiology in the University of Pennsylvania. In one handsome 12mo. volume of 199 pages, with 32 illustrations. Cloth, $1.50.

MAISCH, JOHN M., Phar. D.,

Professor of Materia Medica and Botany in the Philadelphia College of Pharmacy.

A Manual of Organic Materia Medica; Being a Guide to Materia Medica of the Vegetable and Animal Kingdoms. For the use of Students, Druggists, Pharmacists and Physicians. New (second) edition. In one handsome royal 12mo. volume of 550 pages, with 242 illustrations. Cloth, $3.00. *Just ready.*

This work contains the substance,—the *practical* "kernel of the nut" picked out, so that the student has no superfluous labor. He can confidently accept what this work places before him, without any fear that the gist of the matter is not in it. Another merit is that the drugs are placed before him in such a manner as to simplify very much the study of them, enabling the mind to grasp them more readily. The illustrations are most excellent, being very true to nature, and are alone worth the price of the book to the student. To the practical physician and pharmacist it is a valuable work for handy reference and for keeping fresh in the memory the knowledge of materia medica and botany already acquired. We can and do heartily recommend it.—*Medical and Surgical Reporter*, Feb. 14, 1885.

BRUCE, J. MITCHELL, M. D., F. R. C. P.,

Physician and Lecturer on Materia Medica and Therapeutics at Charing Cross Hospital, London.

Materia Medica and Therapeutics. An Introduction to Rational Treatment. In one pocket-size 12mo. volume of 555 pages. Limp cloth, $1.50. *Just ready.* See *Students' Series of Manuals*, page 3.

GRIFFITH, ROBERT EGLESFIELD, M. D.

A Universal Formulary, containing the Methods of Preparing and Administering Officinal and other Medicines. The whole adapted to Physicians and Pharmaceutists. Third edition, thoroughly revised, with numerous additions, by JOHN M. MAISCH, Phar. D., Professor of Materia Medica and Botany in the Philadelphia College of Pharmacy. In one octavo volume of 775 pages, with 38 illustrations. Cloth, $4.50; leather, $5.50.

STILLÉ, A., M. D., LL. D., & MAISCH, J. M., Phar. D.,

Professor Emeritus of the Theory and Practice of Medicine and of Clinical Medicine in the University of Pennsylvania.

Prof. of Mat. Med. and Botany in Phila. College of Pharmacy, Sec'y to the American Pharmaceutical Association.

The National Dispensatory: Containing the Natural History, Chemistry, Pharmacy, Actions and Uses of Medicines, including those recognized in the Pharmacopœias of the United States, Great Britain and Germany, with numerous references to the French Codex. Third edition, thoroughly revised and greatly enlarged. In one magnificent imperial octavo volume of 1767 pages, with 311 fine engravings. Cloth, $7.25; leather, $8.00; half Russia, open back, $9.00. With Denison's "Ready Reference Index" $1.00 in addition to price.in any of above styles of binding. *Just ready.*

In the present revision the authors have labored incessantly with the view of making the third edition of THE NATIONAL DISPENSATORY an even more complete representative of the pharmaceutical and therapeutic science of 1884 than its first edition was of that of 1879. For this, ample material has been afforded not only by the new United States Pharmacopœia, but by those of Germany and France, which have recently appeared and have been incorporated in the Dispensatory, together with a large number of new nonofficinal remedies. It is thus rendered the representative of the most advanced state of American, English, French and German pharmacology and therapeutics. The vast amount of new and important material thus introduced may be gathered from the fact that the additions to this edition amount in themselves to the matter of an ordinary full-sized octavo volume, rendering the work larger by twenty-five per cent. than the last edition. The Therapeutic Index (a feature peculiar to this work), so suggestive and convenient to the practitioner, contains 1600 more references than the last edition—the General Index 3700 more, making the total number of references 22,390, while the list of illustrations has been increased by 80. Every effort has been made to prevent undue enlargement of the volume by having in it nothing that could be regarded as superfluous, yet care has been taken that nothing should be omitted which a pharmacist or physician could expect to find in it.

The appearance of the work has been delayed by nearly a year in consequence of the determination of the authors that it should attain as near an approach to absolute accuracy as is humanly possible. With this view an elaborate and laborious series of examinations and tests have been made to verify or correct the statements of the Pharmacopœia, and very numerous corrections have been found necessary. It has thus been rendered indispensable to all who consult the Pharmacopœia.

The work is therefore presented in the full expectation that it will maintain the position universally accorded to it as the standard authority in all matters pertaining to its subject, as registering the furthest advance of the science of the day, and as embodying in a shape for convenient reference the recorded results of human experience in the laboratory, in the dispensing room, and at the bed-side.

Comprehensive in scope, vast in design and splendid in execution, The National Dispensatory may be justly regarded as the most important work of its kind extant.—*Louisville Medical News*, Dec. 6, 1884.

We have much pleasure in recording the appearance of a third edition of this excellent work of reference. It is an admirable abstract of all that relates to chemistry, pharmacy, materia medica, pharmacology and therapeutics. It may be regarded as embodying the Pharmacopœias of the civilized nations of the world, all being brought up to date. The work has been very well done, a large number of extra-pharmacopœial remedies having been added to those mentioned in previous editions.—*London Lancet*, Nov. 22, 1884.

Its completeness as to subjects, the comprehensiveness of its descriptive language, the thoroughness of the treatment of the topics, its brevity not sacrificing the desirable features of information for which such a work is needed, make this volume a marvel of excellence.—*Pharmaceutical Record*, Aug. 15, 1884.

FARQUHARSON, ROBERT, M. D.,

Lecturer on Materia Medica at St. Mary's Hospital Medical School.

A Guide to Therapeutics and Materia Medica. Third American edition, specially revised by the Author. Enlarged and adapted to the U. S. Pharmacopœia by FRANK WOODBURY, M. D. In one handsome 12mo. volume of 524 pages. Cloth, $2.25.

Dr. Farquharson's Therapeutics is constructed upon a plan which brings before the reader all the essential points with reference to the properties of drugs. It impresses these upon him in such a way as to enable him to take a clear view of the actions of medicines and the disordered conditions in which they must prove useful. The double-columned pages—one side containing the recognized physiological action of the medicine, and the other the disease in which observers (who are nearly always mentioned) have obtained from it good results—make a very good arrangement. The early chapter containing rules for prescribing is excellent.—*Canada Med. and Surg. Journal*, Dec. 1882.

STILLÉ, ALFRED, M. D., LL. D.,

Professor of Theory and Practice of Med. and of Clinical Med. in the Univ. of Penna.

Therapeutics and Materia Medica. A Systematic Treatise on the Action and Uses of Medicinal Agents, including their Description and History. Fourth edition, revised and enlarged. In two large and handsome octavo volumes, containing 1936 pages. Cloth, $10.00; leather, $12.00; very handsome half Russia, raised bands, $13.00.

We can hardly admit that it has a rival in the multitude of its citations and the fulness of its research into clinical histories, and we must assign it a place in the physician's library; not, indeed, as fully representing the present state of knowledge in pharmacodynamics, but as by far the most complete treatise upon the clinical and practical side of the question.—*Boston Medical and Surgical Journal*, Nov. 5, 1874.

COATS, JOSEPH, M. D., F. F. P. S.,

Pathologist to the Glasgow Western Infirmary.

A Treatise on Pathology. In one very handsome octavo volume of 829 pages, with 339 beautiful illustrations. Cloth, $5.50; leather, $6.50.

The work before us treats the subject of Pathology more extensively than it is usually treated in similar works. Medical students as well as physicians, who desire a work for study or reference, that treats the subjects in the various departments in a very thorough manner, but without prolixity, will certainly give this one the preference to any with which we are acquainted. It sets forth the most recent discoveries, exhibits, in an interesting manner, the changes from a normal condition effected in structures by disease, and points out the characteristics of various morbid agencies, so that they can be easily recognized. But, not limited to morbid anatomy, it explains fully how the functions of organs are disturbed by abnormal conditions. There is nothing belonging to its department of medicine that is not as fully elucidated as our present knowledge will admit.—*Cincinnati Medical News*, Oct. 1883.

GREEN, T. HENRY, M. D.,

Lecturer on Pathology and Morbid Anatomy at Charing-Cross Hospital Medical School, London.

Pathology and Morbid Anatomy. Fifth American from the sixth revised and enlarged English edition. In one very handsome octavo volume of 482 pages, with 150 fine engravings. Cloth, $2.50.

The fact that this well-known treatise has so rapidly reached its sixth edition is a strong evidence of its popularity. The author is to be congratulated upon the thoroughness with which he has prepared this work. It is thoroughly abreast with all the most recent advances in pathology. No work in the English language is so admirably adapted to the wants of the student and practitioner as this, and we would recommend it most earnestly to every one.—*Nashville Journal of Medicine and Surgery*, Nov. 1884.

WOODHEAD, G. SIMS, M. D., F. R. C. P. E.,

Demonstrator of Pathology in the University of Edinburgh.

Practical Pathology. A Manual for Students and Practitioners. In one beautiful octavo volume of 497 pages, with 136 exquisitely colored illustrations. Cloth, $6.00.

It forms a real guide for the student and practitioner who is thoroughly in earnest in his endeavor to see for himself and do for himself. To the laboratory student it will be a helpful companion, and all those who may wish to familiarize themselves with modern methods of examining morbid tissues are strongly urged to provide themselves with this manual. The numerous drawings are not fancied pictures, or merely schematic diagrams, but they represent faithfully the actual images seen under the microscope. The author merits all praise for having produced a valuable work.—*Medical Record*, May 31, 1884.

It is manifestly the product of one who has himself travelled over the whole field and who is skilled not merely in the art of histology, but in the observation and interpretation of morbid changes. The work is sure to command a wide circulation. It should do much to encourage the pursuit of pathology, since such advantages in histological study have never before been offered.—*The Lancet*, Jan. 5, 1884.

SCHÄFER, EDWARD A., F. R. S.,

Assistant Professor of Physiology in University College, London.

The Essentials of Histology. In one octavo volume of 246 pages, with 281 illustrations. Cloth, $2.25. *Shortly.*

CORNIL, V., and RANVIER, L.,

Prof. in the Faculty of Med. of Paris. *Prof. in the College of France.*

A Manual of Pathological Histology. Translated, with notes and additions, by E. O. SHAKESPEARE, M. D., Pathologist and Ophthalmic Surgeon to Philadelphia Hospital, and by J. HENRY C. SIMES, M. D., Demonstrator of Pathological Histology in the University of Pennsylvania. In one very handsome octavo volume of 800 pages, with 360 illustrations. Cloth, $5.50; leather, $6.50; half Russia, raised bands, $7.

KLEIN, E., M. D., F. R. S.,

Joint Lecturer on General Anat. and Phys. in the Med. School of St. Bartholomew's Hosp., London.

Elements of Histology. In one pocket-size 12mo. volume of 360 pages, with 181 illus. Limp cloth, red edges, $1.50. See *Students' Series of Manuals*, page 3.

Although an elementary work, it is by no means superficial or incomplete, for the author presents in concise language nearly all the fundamental facts regarding the microscopic structure of tissues. The illustrations are numerous and excellent. We commend Dr. Klein's *Elements* most heartily to the student.—*Medical Record*, Dec. 1, 1883.

PEPPER, A. J., M. B., M. S., F. R. C. S.,

Surgeon and Lecturer at St. Mary's Hospital, London.

Surgical Pathology. In one pocket-size 12mo. volume of 511 pages, with 81 illustrations. Limp cloth, red edges, $2.00. See *Students' Series of Manuals*, page 3.

It is not pretentious, but it will serve exceedingly well as a book of reference. It embodies a great deal of matter, extending over the whole field of surgical pathology. Its form is practical, its language is clear, and the information set forth is well-arranged, well-indexed and well-illustrated. The student will find in it nothing that is unnecessary. The list of subjects covers the whole range of surgery. The book supplies a very manifest want and should meet with success.—*New York Medical Journal*, May 31, 1884.

SCHÄFER'S PRACTICAL HISTOLOGY. In one handsome royal 12mo. volume of 308 pages, with 40 illustrations.

GLUGE'S ATLAS OF PATHOLOGICAL HISTOLOGY. Translated by JOSEPH LEIDY, M. D. In one volume, very large imperial quarto, with 320 copper-plate figures, plain and colored and descriptive letter-press. Cloth, $4.00

FLINT, AUSTIN, M. D.,

Prof. of the Principles and Practice of Med. and of Clin. Med. in Bellevue Hospital Medical College, N. Y.

A Treatise on the Principles and Practice of Medicine. Designed for the use of Students and Practitioners of Medicine. With an Appendix on the Researches of Koch, and their bearing on the Etiology, Pathology, Diagnosis and Treatment of Phthisis. Fifth edition, revised and largely rewritten In one large and closely-printed octavo volume of 1160 pages. Cloth, $5.50; leather, $6.50; half Russia, $7.

Koch's discovery of the bacillus of tubercle gives promise of being the greatest boon ever conferred by science on humanity, surpassing even vaccination in its benefits to mankind. In the appendix to his work, Professor Flint deals with the subject from a practical standpoint, discussing its bearings on the etiology, pathology, diagnosis, prognosis and treatment of pulmonary phthisis. Thus enlarged and completed, this standard work will be more than ever a necessity to the physician who duly appreciates the responsibility of his calling.

A well-known writer and lecturer on medicine recently expressed an opinion, in the highest degree complimentary of the admirable treatise of Dr. Flint, and in eulogizing it, he described it accurately as "readable and reliable." No text-book is more calculated to enchain the interest of the student, and none better classifies the multitudinous subjects included in it. It has already so far won its way in England, that no inconsiderable number of men use it alone in the study of pure medicine; and we can say of it that it is in every way adapted to serve, not only as a complete guide, but also as an ample instructor in the science and practice of medicine. The style of Dr. Flint is always polished and engaging. The work abounds in perspicuous explanation, and is a most valuable text-book of medicine.—*London Medical News.*

This work is so widely known and accepted as the best American text-book of the practice of medicine that it would seem hardly worth while to give this, the fifth edition, anything more than a passing notice. But even the most cursory examination shows that it is, practically, much more than a revised edition; it is, in fact, rather a new work throughout. This treatise will undoubtedly continue to hold the first place in the estimation of American physicians and students. No one of our medical writers approaches Professor Flint in clearness of diction, breadth of view, and, what we regard of transcendent importance, rational estimate of the value of remedial agents. It is thoroughly *practical*, therefore pre-eminently *the book* for American readers.—*St. Louis Clin. Rec.*, Mar. '81.

HARTSHORNE, HENRY, M. D., LL. D.,

Lately Professor of Hygiene in the University of Pennsylvania.

Essentials of the Principles and Practice of Medicine. A Handbook for Students and Practitioners. Fifth edition, thoroughly revised and rewritten. In one royal 12mo. volume of 669 pages, with 144 illustrations. Cloth, $2.75; half bound, $3.00.

Within the compass of 600 pages it treats of the history of medicine, general pathology, general symptomatology, and physical diagnosis (including laryngoscope, ophthalmoscope, etc.), general therapeutics, nosology, and special pathology and practice. There is a wonderful amount of information contained in this work, and it is one of the best of its kind that we have seen.—*Glasgow Medical Journal*, Nov. 1882.

An indispensable book. No work ever exhibited a better average of actual practical treatment than this one; and probably not one writer in our day had a better opportunity than Dr. Hartshorne for condensing all the views of eminent practitioners into a 12mo. The numerous illustrations will be very useful to students especially. These essentials, as the name suggests, are not intended to supersede the text-books of Flint and Bartholow, but they are the most valuable in affording the means to see at a glance the whole literature of any disease, and the most valuable treatment.—*Chicago Medical Journal and Examiner*, April, 1882.

BRISTOWE, JOHN SYER, M. D., F. R. C. P.,

Physician and Joint Lecturer on Medicine at St. Thomas' Hospital.

A Treatise on the Practice of Medicine. Second American edition, revised by the Author. Edited, with additions, by JAMES H. HUTCHINSON, M.D., physician to the Pennsylvania Hospital. In one handsome octavo volume of 1085 pages, with illustrations. Cloth, $5.00; leather, $6.00; very handsome half Russia, raised bands, $6.50.

The reader will find every conceivable subject connected with the practice of medicine ably presented, in a style at once clear, interesting and concise. The additions made by Dr. Hutchinson are appropriate and practical, and greatly add to its usefulness to American readers.—*Buffalo Medical and Surgical Journal*, March, 1880.

WATSON, SIR THOMAS, M. D.,

Late Physician in Ordinary to the Queen.

Lectures on the Principles and Practice of Physic. A new American from the fifth English edition. Edited, with additions, and 190 illustrations, by HENRY HARTSHORNE, A. M., M. D., late Professor of Hygiene in the University of Pennsylvania. In two large octavo volumes of 1840 pages. Cloth, $9.00; leather, $11.00.

LECTURES ON THE STUDY OF FEVER. By A. HUDSON, M. D., M. R. I. A. In one octavo volume of 308 pages. Cloth, $2.50.

STOKES' LECTURES ON FEVER. Edited by John William Moore, M. D., F. K. Q. C. P. In one octavo volume of 280 pages. Cloth, $2.00.

A TREATISE ON FEVER. By ROBERT D. LYONS, K. C. C. In one 8vo. vol. of 354 pp. Cloth, $2.25.

LA ROCHE ON YELLOW FEVER, considered in its Historical, Pathological, Etiological and Therapeutical Relations. In two large and handsome octavo volumes of 1468 pp. Cloth, $7.00.

A CENTURY OF AMERICAN MEDICINE, 1776—1876. By Drs. E. H. CLARKE, H. J. BIGELOW, S. D. GROSS, T. G. THOMAS, and J. S. BILLINGS. In one 12mo. volume of 370 pages. Cloth, $2.25.

For Sale by Subscription Only.

A System of Practical Medicine.

BY AMERICAN AUTHORS.

EDITED BY WILLIAM PEPPER, M. D., LL. D.,

PROVOST AND PROFESSOR OF THE THEORY AND PRACTICE OF MEDICINE AND OF CLINICAL MEDICINE IN THE UNIVERSITY OF PENNSYLVANIA,

Assisted by LOUIS STARR, M. D., Clinical Professor of the Diseases of Children in the Hospital of the University of Pennsylvania.

In five imperial octavo volumes, containing about 1100 *pages each, with illustrations. Price per volume, cloth,* $5; *leather,* $6; *half Russia, raised bands and open back,* $7. *Volume I.* (General Pathology, Sanitary Science and General Diseases) *contains* 1094 *pages, with* 24 *illustrations and is just ready. Volume II.* (General Diseases [continued] and Diseases of the Digestive System) *contains* 1312 *pages, with* 27 *illustrations, and is just ready. Volume III.* (Diseases of the Respiratory, Circulatory and Hæmatopoietic Systems) *containing about* 1050 *pages, will be ready October* 1*st, and the subsequent volumes at intervals of four months thereafter.*

The publishers feel pardonable pride in announcing this magnificent work. For three years it has been in active preparation, and it is now in a sufficient state of forwardness to justify them in calling the attention of the profession to it as the work in which for the first time American medicine is thoroughly represented by its worthiest teachers, and presented in the full development of the practical utility which is its preëminent characteristic. The most able men—from the East and the West, from the North and the South, from all the prominent centres of education, and from all the hospitals which afford special opportunities of study and practice—have united in generous rivalry to bring together this vast aggregate of specialized experience.

The distinguished editor has so apportioned the work that each author has had assigned to him the subject which he is peculiarly fitted to discuss, and in which his views will be accepted as the latest expression of scientific and practical knowledge. The practitioner will therefore find these volumes a complete, authoritative and unfailing work of reference, to which he may at all times turn with full certainty of finding what he needs in its most recent aspect, whether he seeks information on the general principles of medicine, or minute guidance in the treatment of special disease. So wide is the scope of the work that, with the exception of midwifery and matters strictly surgical, it embraces the whole domain of medicine, including the departments for which the physician is accustomed to rely on special treatises, such as diseases of women and children, of the genito-urinary organs, of the skin, of the nerves, hygiene and sanitary science, and medical ophthalmology and otology. Moreover, authors have inserted the formulas which they have found most efficient in the treatment of the various affections. It may thus be truly regarded as a COMPLETE LIBRARY OF PRACTICAL MEDICINE, and the general practitioner possessing it may feel secure that he will require little else in the daily round of professional duties.

In spite of every effort to condense the vast amount of practical information furnished, it has been impossible to present it in less than 5 large octavo volumes, containing about 5500 beautifully printed pages, and embodying the matter of about 15 ordinary octavos. Illustrations are introduced wherever they serve to elucidate the text.

As material for the work is substantially complete in the hands of the editor, the profession may confidently await the appearance of the remaining volumes upon the dates above specified. A detailed prospectus of the work will be sent to any address on application to the publishers.

It is a large undertaking, but quite justifiable in the case of a progressive nation like the United States. At any rate, if we may judge of future volumes from the first, it will be justified by the result. We have nothing but praise to bestow upon the work. The articles are the work of writers, many of whom are already recognized in this country as authorities on the particular topics on which they deal, whilst the others show by the way they have handled their subjects that they are fully equal to the task they had undertaken. * * * A work which we cannot doubt will make a lasting reputation for itself.—*London Medical Times and Gazette,* May 9, 1885.

REYNOLDS, J. RUSSELL, M. D.,

Professor of the Principles and Practice of Medicine in University College, London.

A System of Medicine. With notes and additions by HENRY HARTSHORNE, A. M., M. D., late Professor of Hygiene in the University of Pennsylvania. In three large and handsome octavo volumes, containing 3056 double-columned pages, with 317 illustrations. Price per volume, cloth, $5.00; sheep, $6.00; very handsome half Russia, raised bands, $6.50. Per set, cloth, $15; leather, $18; half Russia, $19.50. *Sold only by subscription.*

STILLÉ, ALFRED, M. D., LL. D.,

Professor Emeritus of the Theory and Practice of Med. and of Clinical Med. in the Univ. of Penna.

Cholera: Its Origin, History, Causation, Symptoms, Lesions, Prevention and Treatment. In one handsome 12mo. volume of 163 pages, with a chart. Cloth, $1.25. *Just ready.*

The threatened importation of cholera into the country renders peculiarly timely this work of an authority upon the subject so eminent as Professor Stillé. The history of previous epidemics, their modes of propagation, the vast recent additions to our knowledge of the causation, prevention and treatment of the disease, all have been handled so skilfully as to present with brevity the information which every practitioner should possess in advance of a visitation.

This timely little work is full of the learning and good judgment which marks all that comes from the pen of its distinguished author. What he has to say on treatment is characterized by his usual caution and his well-known preference for a rational system. Altogether, the monograph is one that will have an excellent influence on the professional mind.—*Medical and Surgical Reporter*, August 1, 1885. q.

FLINT, AUSTIN, M. D.

Clinical Medicine. A Systematic Treatise on the Diagnosis and Treatment of Diseases. Designed for Students and Practitioners of Medicine. In one large and handsome octavo volume of 799 pages. Cloth, $4.50; leather, $5.50; half Russia, $6.00.

It is here that the skill and learning of the great clinician are displayed. He has given us a storehouse of medical knowledge, excellent for the student, convenient for the practitioner, the result of a long life of the most faithful clinical work, collected by an energy as vigilant and systematic as untiring, and weighed by a judgment no less clear than his observation is close.—*Archives of Medicine*, Dec. 1879.

To give an adequate and useful conspectus of the extensive field of modern clinical medicine is a task of no ordinary difficulty; but to accomplish this consistently with brevity and clearness, the different subjects and their several parts receiving the attention which, relatively to their importance, medical opinion claims for them, is still more difficult. This task, we feel bound to say, has been executed with more than partial success by Dr. Flint, whose name is already familiar to students of advanced medicine in this country as that of the author of two works of great merit on special subjects, and of numerous papers exhibiting much originality and extensive research.—*The Dublin Journal*, Dec. 1879.

By the Same Author.

Essays on Conservative Medicine and Kindred Topics. In one very handsome royal 12mo. volume of 210 pages. Cloth, $1.38.

BROADBENT, W. H., M. D., F. R. C. P.,

Physician to and Lecturer on Medicine at St. Mary's Hospital.

The Pulse. In one 12mo. volume. See *Series of Clinical Manuals*, page 3.

SCHREIBER, DR. JOSEPH.

A Manual of Treatment by Massage and Methodical Muscle Exercise. Translated by WALTER MENDELSON, M. D., of New York. In one handsome octavo volume of about 300 pages, with about 125 fine engravings. *Preparing.*

FINLAYSON, JAMES, M. D., Editor,

Physician and Lecturer on Clinical Medicine in the Glasgow Western Infirmary, etc.

Clinical Diagnosis. A Handbook for Students and Practitioners of Medicine. With Chapters by Prof. Gairdner on the Physiognomy of Disease; Prof. Stephens on Diseases of the Female Organs; Dr. Robertson on Insanity; Dr. Gemmell on Physical Diagnosis; Dr. Coats on Laryngoscopy and Post-Mortem Examinations, and by the Editor on Case-taking, Family History and Symptoms of Disorder in the Various Systems. In one handsome 12mo. volume of 546 pages, with 85 illustrations. Cloth, $2.63.

FENWICK, SAMUEL, M. D.,

Assistant Physician to the London Hospital.

The Student's Guide to Medical Diagnosis. From the third revised and enlarged English edition. In one very handsome royal 12mo. volume of 328 pages, with 87 illustrations on wood. Cloth, $2.25.

TANNER, THOMAS HAWKES, M. D.

A Manual of Clinical Medicine and Physical Diagnosis. Third American from the second London edition. Revised and enlarged by TILBURY FOX, M. D. In one small 12mo. volume of 362 pages, with illustrations. Cloth, $1.50.

FOTHERGILL, J. M., M. D., Edin., M. R. C. P., Lond.,

Physician to the City of London Hospital for Diseases of the Chest.

The Practitioner's Handbook of Treatment; Or, The Principles of Therapeutics. New edition. In one octavo volume. *Preparing.*

STURGES' INTRODUCTION TO THE STUDY OF CLINICAL MEDICINE. Being a Guide to the Investigation of Disease. In one handsome 12mo. volume of 127 pages. Cloth, $1.25.

DAVIS' CLINICAL LECTURES ON VARIOUS IMPORTANT DISEASES. By N. S. DAVIS, M. D. Edited by FRANK H. DAVIS, M. D. Second edition. 12mo. 287 pages. Cloth, $1.75.

RICHARDSON, B. W., M.A., M.D., LL. D., F.R.S., F.S.A.

Fellow of the Royal College of Physicians, London.

Preventive Medicine. In one octavo volume of 729 pages. Cloth, $4; leather, $5; very handsome half Russia, raised bands, $5.50.

Dr. Richardson has succeeded in producing a work which is elevated in conception, comprehensive in scope, scientific in character, systematic in arrangement, and which is written in a clear, concise and pleasant manner. He evinces the happy faculty of extracting the pith of what is known on the subject, and of presenting it in a most simple, intelligent and practical form. There is perhaps no similar work written for the general public that contains such a complete, reliable and instructive collection of data upon the diseases common to the race, their origins, causes, and the measures for their prevention. The descriptions of diseases are clear, chaste and scholarly; the discussion of the question of disease is comprehensive, masterly and fully abreast with the latest and best knowledge on the subject, and the preventive measures advised are accurate, explicit and reliable.—*The American Journal of the Medical Sciences*, April, 1884.

This is a book that will surely find a place on the table of every progressive physician. To the medical profession, whose duty is quite as much to prevent as to cure disease, the book will be a boon. —*Boston Medical and Surgical Journal*, Mar. 6, 1884.

The treatise contains a vast amount of solid, valuable hygienic information.—*Medical and Surgical Reporter*, Feb. 23, 1884.

BARTHOLOW, ROBERTS, A. M., M. D., LL. D.,

Prof. of Materia Medica and General Therapeutics in the Jefferson Med. Coll. of Phila., etc.

Medical Electricity. A Practical Treatise on the Applications of Electricity to Medicine and Surgery. Second edition. In one very handsome octavo volume of 292 pages, with 109 illustrations. Cloth, $2.50.

The second edition of this work following so soon upon the first would in itself appear to be a sufficient announcement; nevertheless, the text has been so considerably revised and condensed, and so much enlarged by the addition of new matter, that we cannot fail to recognize a vast improvement upon the former work. The author has prepared his work for students and practitioners—for those who have never acquainted themselves with the subject, or, having done so, find that after a time their knowledge needs refreshing. We think he has accomplished this object. The book is not too voluminous, but is thoroughly practical, simple, complete and comprehensible. It is, moreover, replete with numerous illustrations of instruments, appliances, etc.—*Medical Record*, November 15, 1882.

A most excellent work, addressed by a practitioner to his fellow-practitioners, and therefore thoroughly practical. The work now before us has the exceptional merit of clearly pointing out where the benefits to be derived from electricity must come. It contains all and everything that the practitioner needs in order to understand intelligently the nature and laws of the agent he is making use of, and for its proper application in practice. In a condensed, practical form, it presents to the physician all that he would wish to remember after perusing a whole library on medical electricity, including the results of the latest investigations. It is the book for the practitioner, and the necessity for a second edition proves that it has been appreciated by the profession.—*Physician and Surgeon*, Dec. 1882.

THE YEAR-BOOK OF TREATMENT.

A Comprehensive and Critical Review for Practitioners of Medicine. In one 12mo. volume of 320 pages, bound in limp cloth, with red edges, $1.25.

This work presents to the practitioner not only a complete classified account of all the more important advances made in the treatment of Disease during the year ending Sept. 30, 1884, but also a critical estimate of the same by a competent authority. Each department of practice has been fully and concisely treated, and into the consideration of each subject enter such allusions to recent pathological and clinical work as bear directly upon treatment. As the medical literature of all countries has been placed under contribution, the references given throughout the work, together with the separate indexes of subjects and authors, will serve as a guide for those who desire to investigate any therapeutical topic at greater length.

In a few moments the busy practitioner can refresh his mind as to the principal advances in treatment for a year past. This kind of work is peculiarly useful at the present time, when current literature is teeming with innumerable so-called advances, of which the practitioner has not time to determine the value. Here he has, collected from many sources, a *résumé* of the theories and facts which are new, either entirely or in part, the decision as to their novelty being made by those who by wide reading and long experience are fully competent to render such a verdict.—*American Journal of the Medical Sciences*, April, 1885.

It is a complete account of the more important advances made in the treatment of disease. Extreme pains have been taken to explain clearly in the fewest possible words the views of each writer, and the details of each subject. One of the principle points about the book is its practical, yet concise language. Each editor has well performed his duty, and we can say with truth that it is a volume well worth buying for frequent use. —*Virginia Medical Monthly*, March, 1885.

HABERSHON, S. O., M. D.,

Senior Physician to and late Lect. on Principles and Practice of Med. at Guy's Hospital, London.

On the Diseases of the Abdomen; Comprising those of the Stomach, and other parts of the Alimentary Canal, Œsophagus, Cæcum, Intestines and Peritoneum. Second American from third enlarged and revised English edition. In one handsome octavo volume of 554 pages, with illustrations. Cloth, $3.50.

PAVY'S TREATISE ON THE FUNCTION OF DIGESTION; its Disorders and their Treatment. From the second London edition. In one octavo volume of 238 pages. Cloth, $2.00.

CHAMBERS' MANUAL OF DIET AND REGIMEN IN HEALTH AND SICKNESS. In one handsome octavo volume of 302 pp. Cloth, $2.75.

BARLOW'S MANUAL OF THE PRACTICE OF MEDICINE. With additions by D. F. CONDIE, M. D. 1 vol. 8vo., pp. 603. Cloth, $2.50.

TODD'S CLINICAL LECTURES ON CERTAIN ACUTE DISEASES. In one octavo volume of 320 pages. Cloth, $2.50.

HOLLAND'S MEDICAL NOTES AND REFLECTIONS. 1 vol. 8vo., pp. 493. Cloth, $3.50.

COHEN, J. SOLIS, M. D.,

Lecturer on Laryngoscopy and Diseases of the Throat and Chest in the Jefferson Medical College.

Diseases of the Throat and Nasal Passages. A Guide to the Diagnosis and Treatment of Affections of the Pharynx, Œsophagus, Trachea, Larynx and Nares. Third edition, thoroughly revised and rewritten, with a large number of new illustrations. In one very handsome octavo volume. *Preparing.*

SEILER, CARL, M. D.,

Lecturer on Laryngoscopy in the University of Pennsylvania.

A Handbook of Diagnosis and Treatment of Diseases of the Throat, Nose and Naso-Pharynx. Second edition. In one handsome royal 12mo. volume of 294 pages, with 77 illustrations. Cloth, $1.75.

It is one of the best of the practical text-books on this subject with which we are acquainted. The present edition has been increased in size, but its eminently practical character has been maintained. Many new illustrations have also been introduced, a case-record sheet has been added, and there are a valuable bibliography and a good index of the whole. For any one who wishes to make himself familiar with the practical management of cases of throat and nose disease, the book will be found of great value.—*New York Medical Journal*, June 9, 1883.

The work before us is a concise handbook upon the essentials of diagnosis and treatment in diseases of the throat and nose. The art of laryngoscopy, the anatomy of the throat and nose and the pathology of the mucous membrane are discussed with conciseness and ability. The work is profusely illustrated, excels in many essential features, and deserves a place in the office of the practitioner who would inform himself as to the nature, diagnosis and treatment of a class of diseases almost inseparable from general medical practice. With advanced students the book must be very popular on account of its condensed style. —*Louisville Medical News*, June 26, 1883.

BROWNE, LENNOX, F. R. C. S., Edin.,

Senior Surgeon to the Central London Throat and Ear Hospital, etc.

The Throat and its Diseases. Second American from the second English edition, thoroughly revised. With 100 typical illustrations in colors and 50 wood engravings, designed and executed by the Author. In one very handsome imperial octavo volume of about 350 pages. *Preparing.*

FLINT, AUSTIN, M. D.,

Professor of the Principles and Practice of Medicine in Bellevue Hospital Medical College, N. Y.

A Manual of Auscultation and Percussion; Of the Physical Diagnosis of Diseases of the Lungs and Heart, and of Thoracic Aneurism. Third edition. In one handsome royal 12mo. volume of 240 pages. Cloth, $1.63.

It is safe to say that there is not in the English language, or any other, the equal amount of clear, exact and comprehensible information touching the physical exploration of the chest, in an equal number of words. Professor Flint's language is precise and simple, conveying without dubiety the results of his careful study and ample experience in such wise that the young will find it the best source of instruction, and the old the most pleasant means of reviving and complementing their knowledge.—*American Practitioner*, June, 1883.

BY THE SAME AUTHOR.

Physical Exploration of the Lungs by Means of Auscultation and Percussion. Three lectures delivered before the Philadelphia County Medical Society, 1882–83. In one handsome small 12mo. volume of 83 pages. Cloth, $1.00.

A Practical Treatise on the Physical Exploration of the Chest and the Diagnosis of Diseases Affecting the Respiratory Organs. Second and revised edition. In one handsome octavo volume of 591 pages. Cloth, $4.50.

Phthisis: Its Morbid Anatomy, Etiology, Symptomatic Events and Complications, Fatality and Prognosis, Treatment and Physical Diagnosis; In a series of Clinical Studies. In one handsome octavo volume of 442 pages. Cloth, $3.50.

A Practical Treatise on the Diagnosis, Pathology and Treatment of Diseases of the Heart. Second revised and enlarged edition. In one octavo volume of 550 pages, with a plate. Cloth, $4.

GROSS, S. D., M.D., LL.D., D.C.L. Oxon., LL.D. Cantab.

A Practical Treatise on Foreign Bodies in the Air-passages. In one octavo volume of 452 pages, with 59 illustrations. Cloth, $2.75.

FULLER ON DISEASES OF THE LUNGS AND AIR-PASSAGES. Their Pathology, Physical Diagnosis, Symptoms and Treatment. From the second and revised English edition. In one octavo volume of 475 pages. Cloth, $3.50.

SLADE ON DIPHTHERIA; its Nature and Treatment, with an account of the History of its Prevalence in various Countries. Second and revised edition. In one 12mo. vol., pp. 158. Cloth, $1.25.

WALSHE ON THE DISEASES OF THE HEART AND GREAT VESSELS. Third American edition. In 1 vol. 8vo., 416 pp. Cloth, $3.00.

SMITH ON CONSUMPTION; its Early and Remediable Stages. 1 vol. 8vo., pp. 253. Cloth, $2.25.

LA ROCHE ON PNEUMONIA. 1 vol. 8vo. of 490 pages. Cloth, $3.00.

WILLIAMS ON PULMONARY CONSUMPTION; its Nature, Varieties and Treatment. With an analysis of one thousand cases to exemplify its duration. In one 8vo. vol. of 303 pp. Cloth, $2.50.

JONES' CLINICAL OBSERVATIONS ON FUNCTIONAL NERVOUS DISORDERS. Second American edition. In one handsome octavo volume of 340 pages. Cloth, $3.25.

MITCHELL, S. WEIR, M. D.,

Physician to Orthopædic Hospital and the Infirmary for Diseases of the Nervous System, Phila., etc.

Lectures on Diseases of the Nervous System; Especially in Women. Second edition. In one 12mo. volume of 288 pages. Cloth, $1.75. *Just ready.*

We feel sure that the new edition of Dr. Mitchell's admirable lectures will be received on this side of the Atlantic with more than ordinary attention. His subject, the nervous disorders of women, is one that interests every practitioner, and his views on treatment are gradually receiving general acceptance.—*London Medical Times and Gazette*, July 4, 1885.

ROSS, JAMES, M. D., F. R. C. P., LL. D.,

Senior Assistant Physician to the Manchester Royal Infirmary.

A Text-Book on Diseases of the Nervous System. In one handsome octavo volume of 600 pages, fully illustrated. *Shortly.*

HAMILTON, ALLAN McLANE, M. D.,

Attending Physician at the Hospital for Epileptics and Paralytics, Blackwell's Island, N. Y.

Nervous Diseases; Their Description and Treatment. Second edition, thoroughly revised and rewritten. In one octavo volume of 598 pages, with 72 illustrations. Cloth, $4.

When the first edition of this good book appeared we gave it our emphatic endorsement, and the present edition enhances our appreciation of the book and its author as a safe guide to students of clinical neurology. One of the best and most critical of English neurological journals, *Brain*, has characterized this book as the best of its kind in any language, which is a handsome endorsement from an exalted source. The improvements in the new edition, and the additions to it, will justify its purchase even by those who possess the old.—*Alienist and Neurologist*, April, 1882.

TUKE, DANIEL HACK, M. D.,

Joint Author of The Manual of Psychological Medicine, etc.

Illustrations of the Influence of the Mind upon the Body in Health and Disease. Designed to elucidate the Action of the Imagination. New edition. Thoroughly revised and rewritten. In one handsome octavo volume of 467 pages, with two colored plates. Cloth, $3.00.

It is impossible to peruse these interesting chapters without being convinced of the author's perfect sincerity, impartiality, and thorough mental grasp. Dr. Tuke has exhibited the requisite amount of scientific address on all occasions, and the more intricate the phenomena the more firmly has he adhered to a physiological and rational method of interpretation. Guided by an enlightened deduction, the author has reclaimed for science a most interesting domain in psychology, previously abandoned to charlatans and empirics. This book, well conceived and well written, must commend itself to every thoughtful understanding.—*New York Medical Journal*, September 6, 1884.

CLOUSTON, THOMAS S., M. D., F. R. C. P., L. R. C. S.,

Lecturer on Mental Diseases in the University of Edinburgh.

Clinical Lectures on Mental Diseases. With an Appendix, containing an Abstract of the Statutes of the United States and of the Several States and Territories relating to the Custody of the Insane. By CHARLES F. FOLSOM, M. D., Assistant Professor of Mental Diseases, Medical Department of Harvard University. In one handsome octavo volume of 541 pages, illustrated with eight lithographic plates, four of which are beautifully colored. Cloth, $4.

The practitioner as well as the student will accept the plain, practical teaching of the author as a forward step in the literature of insanity. It is refreshing to find a physician of Dr. Clouston's experience and high reputation giving the bedside notes upon which his experience has been founded and his mature judgment established. Such clinical observations cannot but be useful to the general practitioner in guiding him to a diagnosis and indicating the treatment, especially in many obscure and doubtful cases of mental disease. To the American reader Dr. Folsom's *Appendix* adds greatly to the value of the work, and will make it a desirable addition to every library. —*American Psychological Journal*, July, 1884.

☞ Dr. Folsom's *Abstract* may also be obtained separately in one octavo volume of 108 pages. Cloth, $1.50.

SAVAGE, GEORGE H., M. D.,

Lecturer on Mental Diseases at Guy's Hospital, London.

Insanity and Allied Neuroses, Practical and Clinical. In one 12mo. volume of 551 pages, with 18 typical illustrations. Cloth, $2.00. *Just ready.* See *Series of Clinical Manuals*, page 3.

As a handbook, a guide to practitioners and students, the book fulfils an admirable purpose. The many forms of insanity are described with characteristic clearness, the illustrative cases are carefully selected, and as regards treatment, sound common sense is everywhere apparent. We repeat that Dr. Savage has written an excellent manual for the practitioner and student.—*American Journal of Insanity*, April, 1885.

PLAYFAIR, W. S., M. D., F. R. C. P.,

The Systematic Treatment of Nerve Prostration and Hysteria. In one handsome small 12mo. volume of 97 pages. Cloth, $1.00.

Blandford on Insanity and its Treatment: Lectures on the Treatment, Medical and Legal, of Insane Patients. In one very handsome octavo volume.

GROSS, S. D., M. D., LL. D., D. C. L. Oxon., LL. D. Cantab.,

Emeritus Professor of Surgery in the Jefferson Medical College of Philadelphia.

A System of Surgery: Pathological, Diagnostic, Therapeutic and Operative. Sixth edition, thoroughly revised and greatly improved. In two large and beautifully-printed imperial octavo volumes containing 2382 pages, illustrated by 1623 engravings. Strongly bound in leather, raised bands, $15; half Russia, raised bands, $16.

Dr. Gross' *System of Surgery* has long been the standard work on that subject for students and practitioners.—*London Lancet*, May 10, 1884.

The work as a whole needs no commendation. Many years ago it earned for itself the enviable reputation of the leading American work on surgery, and it is still capable of maintaining that standard. The reason for this need only be mentioned to be appreciated. The author has always been calm and judicious in his statements, has based his conclusions on much study and personal experience, has been able to grasp his subject in its entirety, and, above all, has conscientiously adhered to truth and fact, weighing the evidence, *pro* and *con*, accordingly. A considerable amount of new material has been introduced, and altogether the distinguished author has reason to be satisfied that he has placed the work fully abreast of the state of our knowledge.—*Med. Record*, Nov. 18, 1882.

His *System of Surgery*, which, since its first edition in 1859, has been a standard work in this country as well as in America, in "the whole domain of surgery," tells how earnest and laborious and wise a surgeon he was, how thoroughly he appreciated the work done by men in other countries, and how much he contributed to promote the science and practice of surgery in his own. There has been no man to whom America is so much indebted in this respect as the Nestor of surgery.—*British Medical Journal*, May 10, 1884.

ASHHURST, JOHN, Jr., M. D.,

Professor of Clinical Surgery, Univ. of Penna., Surgeon to the Episcopal Hospital, Philadelphia.

The Principles and Practice of Surgery. Fourth edition, enlarged and revised. In one large and handsome octavo volume of about 1100 pages, with about 575 illustrations. *Shortly.*

GOULD, A. PEARCE, M. S., M. B., F. R. C. S.,

Assistant Surgeon to Middlesex Hospital.

Elements of Surgical Diagnosis. In one pocket-size 12mo. volume of 589 pages. Cloth, $2.00. *Just ready.* See *Students' Series of Manuals*, page 3.

The student and practitioner will find the principles of surgical diagnosis very satisfactorily set forth with all unnecessary verbiage eliminated. Every medical student attending lectures should have a copy to study during the intervals, and if practitioners would devote a portion of their leisure to the study of it, they would receive immense benefit in the way of refreshing their knowledge and bringing it up to the present state of progress.—*Cincinnati Medical News*, Jan., 1885.

GIBNEY, V. P., M. D.,

Surgeon to the Orthopædic Hospital, New York, etc.

Orthopædic Surgery. For the use of Practitioners and Students. In one handsome octavo volume, profusely illustrated. *Preparing.*

ROBERTS, JOHN B., A. M., M. D.,

Lecturer on Anatomy and on Operative Surgery at the Philadelphia School of Anatomy.

The Principles and Practice of Surgery. For the use of Students and Practitioners of Medicine and Surgery. In one very handsome octavo volume of about 500 pages, with many illustrations. *Preparing.*

BELLAMY, EDWARD, F. R. C. S.,

Surgeon and Lecturer on Surgery at Charing Cross Hospital, London.

Operative Surgery. *Shortly.* See *Students' Series of Manuals*, page 3.

STIMSON, LEWIS A., B. A., M. D.,

Prof. of Pathol. Anat. at the Univ. of the City of New York, Surgeon and Curator to Bellevue Hosp.

A Manual of Operative Surgery. New (second) edition. In one very handsome royal 12mo. volume of about 500 pages, with about 350 illustrations. Cloth, $2.50. *Shortly.*

A notice of the previous edition is appended.

This volume is devoted entirely to operative surgery, and is intended to familiarize the student with the details of operations and the different modes of performing them. The work is handsomely illustrated, and the descriptions are clear and well-drawn. It is a clever and useful volume; every student should possess one. This work does away with the necessity of pondering over larger works on surgery for descriptions of operations, as it presents in a nutshell what is wanted by the surgeon without an elaborate search to find it.—*Maryland Medical Journal*, August, 1878.

SARGENT ON BANDAGING AND OTHER OPERATIONS OF MINOR SURGERY. New edition, with a Chapter on military surgery. One 12mo. volume of 383 pages, with 187 cuts. Cloth, $1.75.

MILLER'S PRINCIPLES OF SURGERY. Fourth American from the third Edinburgh edition. In one 8vo. vol. of 638 pages, with 340 illustrations. Cloth, $3.75..

MILLER'S PRACTICE OF SURGERY. Fourth and revised American from the last Edinburgh edition. In one large 8vo. vol. of 682 pages, with 364 illustrations. Cloth, $6.75.

PIRRIE'S PRINCIPLES AND PRACTICE OF SURGERY. Edited by JOHN NEILL, M. D. In one 8vo. vol. of 784 pp. with 316 illus. Cloth, $3.75.

COOPER'S LECTURES ON THE PRINCIPLES AND PRACTICE OF SURGERY. In one 8vo. vol. of 767 pages. Cloth, $2.00.

SKEY'S OPERATIVE SURGERY. In one vol. 8vo. of 661 pages, with 81 woodcuts. Cloth, $3.25.

GIBSON'S INSTITUTES AND PRACTICE OF SURGERY. Eighth edition. In two octavo vols. of 965 pages, with 34 plates. Leather $6.50.

ERICHSEN, JOHN E., F. R. S., F. R. C. S.,

Professor of Surgery in University College, London, etc.

The Science and Art of Surgery; Being a Treatise on Surgical Injuries, Diseases and Operations. From the eighth and enlarged English edition. In two large and beautiful octavo volumes of 2316 pages, illustrated with 984 engravings on wood. Cloth, $9; leather, raised bands, $11; half Russia, raised bands, $12. *Just ready.*

After the profession has placed its approval upon a work to the extent of purchasing seven editions, it does not need to be introduced. Simultaneous with the appearance of this edition a translation is being made into Italian and Spanish. Thus this favorite text-book on surgery holds its own in spite of numerous rivals at the end of thirty years. It is a grand book, worthy of the art in the interest of which it is written.—*Detroit Lancet*, Jan. 10, 1885.

After being before the profession for thirty years and maintaining during that period a reputation as a leading work on surgery, there is not much to be said in the way of comment or criticism. That it still holds its own goes without saying. The author infuses into it his large experience and ripe judgment. Wedded to no school, committed to no theory, biassed by no hobby, he imparts an honest personality in his observations, and his teachings are the rulings of an impartial judge. Such men are always safe guides, and their works stand the tests of time and experience. Such an author is Erichsen, and such a work is his *Surgery*.—*Medical Record*, Feb. 21, 1885.

BRYANT, THOMAS, F. R. C. S.,

Surgeon and Lecturer on Surgery at Guy's Hospital, London.

The Practice of Surgery. Fourth American from the fourth and revised English edition. In one large and very handsome imperial octavo volume of 1040 pages, with 727 illustrations. Cloth, $6.50; leather, $7.50; half Russia, $8.00. *Just ready.*

The treatise takes in the whole field of surgery, that of the eye, the ear, the female organs, orthopædics, venereal diseases, and military surgery, as well as more common and general topics. All of these are treated with clearness and with sufficient fulness to suit all practical purposes. The illustrations are numerous and well printed. We do not doubt that this new edition will continue to maintain the popularity of this standard work.—*Medical and Surgical Reporter*, Feb. 14, '85.

This most magnificent work upon surgery has reached a fourth edition in this country, showing the high appreciation in which it is held by the American profession. It comes fresh from the pen of the author. That it is the very best work on surgery for medical students we think there can be no doubt. The author seems to have understood just what a student needs, and has prepared the work accordingly.—*Cincinnati Medical News*, January, 1885.

By the same Author.

Diseases of the Breast. In one 12mo. volume. *Preparing.* See *Series of Clinical Manuals*, page 3.

BUTLIN, HENRY T., F. R. C. S.,

Assistant Surgeon to St. Bartholomew's Hospital, London.

Diseases of the Tongue. In one 12mo. volume of 456 pages, with 8 colored plates and 3 woodcuts. Cloth, $3.50. *Just ready.* See *Series of Clinical Manuals*, page 3.

ESMARCH, Dr. FRIEDRICH,

Professor of Surgery at the University of Kiel, etc.

Early Aid in Injuries and Accidents. Five Ambulance Lectures. Translated by H. R. H. PRINCESS CHRISTIAN. In one handsome small 12mo. volume of 109 pages, with 24 illustrations. Cloth, 75 cents.

The course of instruction is divided into five sections or lectures. The first, or introductory lecture, gives a brief account of the structure and organization of the human body, illustrated by clear, suitable diagrams. The second teaches how to give judicious help in ordinary injuries—contusions, wounds, hæmorrhage and poisoned wounds. The third treats of first aid in cases of fracture and of dislocations, in sprains and in burns. Next, the methods of affording first treatment in cases of frost-bite, of drowning, of suffocation, of loss of consciousness and of poisoning are described; and the fifth lecture teaches how injured persons may be most safely and easily transported to their homes, to a medical man, or to a hospital. The illustrations in the book are clear and good.—*Medical Times and Gazette*, Nov. 4, 1882.

TREVES, FREDERICK, F. R. C. S.,

Assistant Surgeon to and Lecturer on Surgery at the London Hospital.

Intestinal Obstruction. In one pocket-size 12mo. volume of 522 pages, with 60 illustrations. Limp cloth, blue edges, $2.00. *Just ready.* See *Series of Clinical Manuals*, page 3.

A standard work on a subject that has not been so comprehensively treated by any contemporary English writer. Its completeness renders a full review difficult, since every chapter deserves minute attention, and it is impossible to do thorough justice to the author in a few paragraphs. *Intestinal Obstruction* is a work that will prove of equal value to the practitioner, the student, the pathologist, the physician and the operating surgeon.—*British Medical Journal*, Jan. 31, 1885.

BALL, CHARLES B., M. Ch., Dub., F. R. C. S. E.,

Surgeon and Teacher at Sir P. Dun's Hospital, Dublin.

Diseases of the Rectum and Anus. In one 12mo. volume of 550 pages. *Preparing.* See *Series of Clinical Manuals*, page 3.

DRUITT, ROBERT, M. R. C. S., etc.

The Principles and Practice of Modern Surgery. From the eighth London edition. In one 8vo. volume of 687 pages, with 432 illus. Cloth, $4; leather, $5.

HOLMES, TIMOTHY, M. A.,

Surgeon and Lecturer on Surgery at St. George's Hospital, London.

A System of Surgery; Theoretical and Practical. IN TREATISES BY VARIOUS AUTHORS. AMERICAN EDITION, THOROUGHLY REVISED AND RE-EDITED by JOHN H. PACKARD, M. D., Surgeon to the Episcopal and St. Joseph's Hospitals, Philadelphia, assisted by a corps of thirty-three of the most eminent American surgeons. In three large and very handsome imperial octavo volumes containing 3137 double-columned pages, with 979 illustrations on wood and 13 lithographic plates, beautifully colored. Price per volume, cloth, $6.00; leather, $7.00; half Russia, $7.50. Per set, cloth, $18.00; leather, $21.00; half Russia, $22.50. *Sold only by subscription.*

VOLUME I. contains GENERAL PATHOLOGY, MORBID PROCESSES, INJURIES IN GENERAL, COMPLICATIONS OF INJURIES AND INJURIES OF REGIONS.

VOLUME II. contains DISEASES OF ORGANS OF SPECIAL SENSE, CIRCULATORY SYSTEM, DIGESTIVE TRACT AND GENITO-URINARY ORGANS.

VOLUME III. contains DISEASES OF THE RESPIRATORY ORGANS, BONES, JOINTS AND MUSCLES, DISEASES OF THE NERVOUS SYSTEM, GUNSHOT WOUNDS, OPERATIVE AND MINOR SURGERY, AND MISCELLANEOUS SUBJECTS (including an essay on HOSPITALS).

This great work, issued some years since in England, has won such universal confidence wherever the language is spoken that its republication here, in a form more thoroughly adapted to the wants of the American practitioner, has seemed to be a duty owing to the profession. To accomplish this, each article has been placed in the hands of a gentleman specially competent to treat its subject, and no labor has been spared to bring each one up to the foremost level of the times, and to adapt it thoroughly to the practice of the country. In certain cases this has rendered necessary the substitution of an entirely new essay for the original, as in the case of the articles on Skin Diseases, on Diseases of the Absorbent System, and on Anæsthetics, in the use of which American practice differs from that of England. The same careful and conscientious revision has been pursued throughout, leading to an increase of nearly one-fourth in matter, while the series of illustrations has been nearly trebled, and the whole is presented as a complete exponent of British and American Surgery, adapted to the daily needs of the working practitioner.

In order to bring it within the reach of every member of the profession, the five volumes of the original have been compressed into three by employing a double-columned royal octavo page, and in this improved form it is offered at less than one-half the price of the original. It is printed and bound to match in every detail with Reynolds' System of Medicine. The work will be sold by subscription only, and in due time every member of the profession will be called upon and offered an opportunity to subscribe.

The authors of the original English edition are men of the front rank in England, and Dr. Packard has been fortunate in securing as his American coadjutors such men as Bartholow, Hyde, Hunt, Conner, Stimson, Morton, Hodgen, Jewell and their colleagues. As a whole, the work will be solid and substantial, and a valuable addition to the library of any medical man. It is more wieldly and more useful than the English edition, and with its companion work—"Reynolds' System of Medicine"—will well represent the present state of our science. One who is familiar with those two works will be fairly well furnished head-wise and hand-wise.—*The Medical News*, Jan. 7, 1882.

STIMSON, LEWIS A., B. A., M. D.,

Professor of Pathological Anatomy at the University of the City of New York, Surgeon and Curator to Bellevue Hospital, Surgeon to the Presbyterian Hospital, New York, etc.

A Practical Treatise on Fractures. In one very handsome octavo volume of 598 pages, with 360 beautiful illustrations. Cloth, $4.75; leather, $5.75.

The author has given to the medical profession in this treatise on fractures what is likely to become a standard work on the subject. It is certainly not surpassed by any work written in the English, or, for that matter, any other language. The author tells us in a short, concise and comprehensive manner, all that is known about his subject. There is nothing scanty or superficial about it, as in most other treatises; on the contrary, everything is thorough. The chapters on repair of fractures and their treatment show him not only to be a profound student, but likewise a practical surgeon and pathologist. His mode of treatment of the different fractures is eminently sound and practical. We consider this work one of the best on fractures; and it will be welcomed not only as a text-book, but also by the surgeon in full practice.—*N. O. Medical and Surgical Journal*, March, 1883.

The author gives in clear language all that the practical surgeon need know of the science of fractures, their etiology, symptoms, processes of union, and treatment, according to the latest developments. On the basis of mechanical analysis the author accurately and clearly explains the clinical features of fractures, and by the same method arrives at the proper diagnosis snd rational treatment. A thorough explanation of the pathological anatomy and a careful description of the various methods of procedure make the book full of value for every practitioner.—*Centralblatt für Chirurgie*, May 19, 1883.

MARSH, HOWARD, F. R. C. S.,

Senior Assistant Surgeon to and Lecturer on Anatomy at St. Bartholomew's Hospital, London.

Diseases of the Joints. In one 12mo. volume. *Preparing.* See *Series of Clinical Manuals*, page 3.

PICK, T. PICKERING, F. R. C. S.,

Surgeon to and Lecturer on Surgery at St. George's Hospital, London.

Fractures and Dislocations. In one 12mo. volume. *Preparing.* See *Series of Clinical Manuals*, page 3.

HAMILTON, FRANK H., M. D., LL. D.,

Surgeon to Bellevue Hospital, New York.

A Practical Treatise on Fractures and Dislocations. Seventh edition, thoroughly revised and much improved. In one very handsome octavo volume of 998 pages, with 379 illustrations. Cloth, $5.50: leather, $6.50; very handsome half Russia, open back, $7.00. *Just ready.*

Hamilton's great experience and wide acquaintance with the literature of the subject have enabled him to complete the labors of Malgaigne and to place the reader in possession of the advances made during thirty years. The editions have followed each other rapidly, and they introduce us to the methods of practice, often so wise, of his American colleagues. More practical than Malgaigne's work, it will serve as a valuable guide to the practitioner in the numerous and embarrassing cases which come under his observation.—*Archives Générales de Médecine*, Paris, Nov. 1884.

This work, which, since its first appearance twenty-five years ago, has gone through many editions, and been much enlarged, may now be fairly regarded as the authoritative book of reference on the subjects of fractures and dislocations. Each successive edition has been rendered of greater value through the addition of more recent work, and especially of the recorded researches and improvements made by the author himself and his countrymen.—*British Medical Journal*, May 9, 1885.

With its first appearance in 1859, this work took rank among the classics in medical literature, and has ever since been quoted by surgeons the world over as an authority upon the topics of which it treats. The surgeon, if one can be found who does not already know the work, will find it scientific, forcible and scholarly in text, exhaustive in detail, and ever marked by a spirit of wise conservatism.—*Louisville Medical News*, Jan. 10, 1885.

For a quarter of a century the author has been elaborating and perfecting his work, so that it now stands as the best of its kind in any language. As a text-book and as a book of reference and guidance for practitioners it is simply invaluable.—*New Orleans Med. and Surg. Journ'l*, Nov. 1884.

JULER, HENRY E., F. R. C. S.,

Senior Ass't Surgeon, Royal Westminster Ophthalmic Hosp.; late Clinical Ass't, Moorfields, London.

A Handbook of Ophthalmic Science and Practice. In one handsome octavo volume of 460 pages, with 125 woodcuts, 27 colored plates, and selections from the Test-types of Jaeger and Snellen. Cloth, $4.50; leather, $5.50. *Just ready.*

This work is distinguished by the great number of colored plates which appear in it for illustrating various pathological conditions. They are very beautiful in appearance, and have been executed with great care as to accuracy. An examination of the work shows it to be one of high standing, one that will be regarded as an authority among ophthalmologists. The treatment recommended is such as the author has learned from actual experience to be the best.—*Cincinnati Medical News*, Dec. 1884.

It presents to the student concise descriptions and typical illustrations of all important eye affections, placed in juxtaposition, so as to be grasped at a glance. Beyond a doubt it is the best illustrated handbook of ophthalmic science which has ever appeared. Then, what is still better, these illustrations are nearly all original. We have examined this entire work with great care, and it represents the commonly accepted views of advanced ophthalmologists. We can most heartily commend this book to all medical students, practitioners and specialists. — *Detroit Lancet*, Jan. 1885.

WELLS, J. SOELBERG, F. R. C. S.,

Professor of Ophthalmology in King's College Hospital, London, etc.

A Treatise on Diseases of the Eye. Fourth American from the third London edition. Thoroughly revised, with copious additions, by CHARLES S. BULL, M.D., Surgeon and Pathologist to the New York Eye and Ear Infirmary. In one large octavo volume of 822 pages, with 257 illustrations on wood, six colored plates, and selections from the Test-types of Jaeger and Snellen. Cloth, $5.00; leather, $6.00; half Russia, $6.50.

The present edition appears in less than three years since the publication of the last American edition, and yet, from the numerous recent investigations that have been made in this branch of medicine, many changes and additions have been required to meet the present scope of knowledge upon this subject. A critical examination at once shows the fidelity and thoroughness with which the editor has accomplished his part of the work. The illustrations throughout are good. This edition can be recommended to all as a complete treatise on diseases of the eye, than which probably none better exists.—*Medical Record*, Aug. 18, '83.

NETTLESHIP, EDWARD, F. R. C. S.,

Ophthalmic Surg. and Lect. on Ophth. Surg. at St. Thomas' Hospital, London.

The Student's Guide to Diseases of the Eye. Second edition. With a chapter on the Detection of Color-Blindness, by WILLIAM THOMSON, M. D., Ophthalmologist to the Jefferson Medical College. In one royal 12mo. volume of 416 pages, with 138 illustrations. Cloth, $2.00.

This admirable guide bids fair to become the favorite text-book on ophthalmic surgery with students and general practitioners. It bears throughout the imprint of sound judgment combined with vast experience. The illustrations are numerous and well chosen. This book, within the short compass of about 400 pages, contains a lucid exposition of the modern aspect of ophthalmic science.—*Medical Record*, June 23, 1883.

BROWNE, EDGAR A.,

Surgeon to the Liverpool Eye and Ear Infirmary and to the Dispensary for Skin Diseases.

How to Use the Ophthalmoscope. Being Elementary Instructions in Ophthalmoscopy, arranged for the use of Students. In one small royal 12mo. volume of 116 pages, with 35 illustrations. Cloth, $1.00.

LAWSON ON INJURIES TO THE EYE, ORBIT AND EYELIDS: Their Immediate and Remote Effects. 8 vo., 404 pp., 92 illus. Cloth, $3.50.

LAURENCE AND MOON'S HANDY BOOK OF OPHTHALMIC SURGERY, for the use of Practitioners. Second edition. In one octavo volume of 227 pages, with 65 illust. Cloth, $2.75.

CARTER'S PRACTICAL TREATISE ON DISEASES OF THE EYE. Edited by JOHN GREEN, M.D. In one handsome octavo volume.

BURNETT, CHARLES H., A. M., M. D.,

Professor of Otology in the Philadelphia Polyclinic; President of the American Otological Society.

The Ear, Its Anatomy, Physiology and Diseases. A Practical Treatise for the use of Medical Students and Practitioners. New (second) edition. In one handsome octavo volume of 580 pages, with 107 illustrations. Cloth, $4.00; leather, $5.00. *Just ready.*

We note with pleasure the appearance of a second edition of this valuable work. When it first came out it was accepted by the profession as one of the standard works on modern aural surgery in the English language; and in his second edition Dr. Burnett has fully maintained his reputation, for the book is replete with valuable information and suggestions. The revision has been carefully carried out, and much new matter added. Dr. Burnett's work must be regarded as a very valuable contribution to aural surgery, not only on account of its comprehensiveness, but because it contains the results of the careful personal observation and experience of this eminent aural surgeon. —*London Lancet*, Feb. 21, 1885.

POLITZER, ADAM,

Imperial-Royal Prof. of Aural Therap. in the Univ. of Vienna.

A Text-Book of the Ear and its Diseases. Translated, at the Author's request, by JAMES PATTERSON CASSELLS, M. D., M. R. C. S. In one handsome octavo volume of 800 pages, with 257 original illustrations. Cloth, $5.50.

The work itself we do not hesitate to pronounce the best upon the subject of aural diseases which has ever appeared, systematic without being too diffuse on obsolete subjects, and eminently practical in every sense. The anatomical descriptions of each separate division of the ear are admirable, and profusely illustrated by woodcuts. They are followed immediately by the physiology of the section, and this again by the pathological physiology, an arrangement which serves to keep up the interest of the student by showing the direct application of what has preceded to the study of disease. The whole work can be recommended as a reliable guide to the student, and an efficient aid to the practitioner in his treatment.—*Boston Medical and Surgical Journal*, June 7, 1883.

ROBERTS, WILLIAM, M. D.,

Lecturer on Medicine in the Manchester School of Medicine, etc.

A Practical Treatise on Urinary and Renal Diseases, including Urinary Deposits. Fourth American from the fourth London edition. In one handsome octavo volume of 609 pages, with 81 illustrations. Cloth, $3.50. *Just ready.*

The peculiar value and finish of the book are derived from its resolute maintenance of a clinical and practical character. This volume is an unrivalled exposition of everything which relates directly or indirectly to the diagnosis, prognosis and treatment of urinary diseases, and possesses a completeness not found elsewhere in our language.—*The Medical Chronicle*, July, 1885. q.

GROSS, S. D., M. D., LL. D., D. C. L., etc.

A Practical Treatise on the Diseases, Injuries and Malformations of the Urinary Bladder, the Prostate Gland and the Urethra. Third edition, thoroughly revised by SAMUEL W. GROSS, M. D., Professor of the Principles of Surgery and of Clinical Surgery in the Jefferson Medical College, Philadelphia. In one octavo volume of 574 pages, with 170 illustrations. Cloth, $4.50.

MORRIS, HENRY, M. B., F. R. C. S.,

Surgeon to and Lecturer on Surgery at Middlesex Hospital, London.

Surgical Diseases of the Kidney. In one 12mo. volume. *Preparing.* See *Series of Clinical Manuals*, page 3.

LUCAS, CLEMENT, M. B., B. S., F. R. C. S.,

Senior Assistant Surgeon to Guy's Hospital, London.

Diseases of the Urethra. In one 12mo. volume. *Preparing.* See *Series of Clinical Manuals*, page 3.

THOMPSON, SIR HENRY,

Surgeon and Professor of Clinical Surgery to University College Hospital, London.

Lectures on Diseases of the Urinary Organs. Second American from the third English edition. In one 8vo. volume of 203 pp., with 25 illustrations. Cloth, $2.25.

By the Same Author.

On the Pathology and Treatment of Stricture of the Urethra and Urinary Fistulæ. From the third English edition. In one octavo volume of 359 pages, with 47 cuts and 3 plates. Cloth, $3.50.

COLEMAN, A., L. R. C. P., F. R. C. S., Exam. L. D. S.,

Senior Dent. Surg. and Lect. on Dent. Surg. at St. Bartholomew's Hosp. and the Dent. Hosp., London.

A Manual of Dental Surgery and Pathology. Thoroughly revised and adapted to the use of American Students, by THOMAS C. STELLWAGEN, M. A., M. D., D. D. S., Prof. of Physiology at the Philadelphia Dental College. In one handsome octavo volume of 412 pages, with 331 illustrations. Cloth, $3.25.

BASHAM ON RENAL DISEASES: A Clinical Guide to their Diagnosis and Treatment. In one 12mo. vol. of 304 pages, with 21 illustrations. Cloth, $2.00.

BUMSTEAD, F. J., M. D., LL. D., and ***TAYLOR, R. W., A. M., M. D.,***

Late Professor of Venereal Diseases at the College of Physicians and Surgeons, New York, etc.

Surgeon to Charity Hospital, New York, Prof. of Venereal and Skin Diseases in the University of Vermont, Pres. of the Am. Dermatological Ass'n.

The Pathology and Treatment of Venereal Diseases. Including the results of recent investigations upon the subject. Fifth edition, revised and largely re-written, by Dr. Taylor. In one large and handsome octavo volume of 898 pages with 139 illustrations, and thirteen chromo-lithographic figures. Cloth, $4.75; leather, $5.75; very handsome half Russia, $6.25.

It is a splendid record of honest labor, wide research, just comparison, careful scrutiny and original experience, which will always be held as a high credit to American medical literature. This is not only the best work in the English language upon the subjects of which it treats, but also one which has no equa. in other tongues for its clear, comprehensive and practical handling of its themes.—*American Journal of the Medical Sciences*, Jan, 1884.

It is certainly the best single treatise on venereal in our own, and probably the best in any language.—*Boston Medical and Surgical Journal*, April 3, 1884.

The character of this standard work is so well known that it would be superfluous here to pass in review its general or special points of excellence. The verdict of the profession has been passed; it has been accepted as the most thorough and complete exposition of the pathology and treatment of venereal diseases in the language. Admirable as a model of clear description, an exponent of sound pathological doctrine, and a guide for rational and successful treatment, it is an ornament to the medical literature of this country. The additions made to the present edition are eminently judicious, from the standpoint of practical utility.—*Journal of Cutaneous and Venereal Diseases*, Jan. 1884.

CORNIL, V.,

Professor to the Faculty of Medicine of Paris, and Physician to the Lourcine Hospital.

Syphilis, its Morbid Anatomy, Diagnosis and Treatment. Specially revised by the Author, and translated with notes and additions by J. HENRY C. SIMES, M. D., Demonstrator of Pathological Histology in the University of Pennsylvania, and J. WILLIAM WHITE, M. D., Lecturer on Venereal Diseases and Demonstrator of Surgery in the University of Pennsylvania. In one handsome octavo volume of 461 pages, with 84 very beautiful illustrations. Cloth, $3.75.

The anatomical and histological characters of the hard and soft sore are admirably described. The multiform cutaneous manifestations of the disease are dealt with histologically in a masterly way, as we should indeed expect them to be, and the accompanying illustrations are executed carefully and well. The various nervous lesions which are the recognized outcome of the syphilitic dyscrasia are treated with care and consideration. Syphilitic epilepsy, paralysis, cerebral syphilis and locomotor ataxia are subjects full of interest; and nowhere in the whole volume is the clinical experience of the author or the wide acquaintance of the translators with medical literature more evident. The anatomy, the histology, the pathology and the clinical features of syphilis are represented in this work in their best, most practical and most instructive form, and no one will rise from its perusal without the feeling that his grasp of the wide and important subject on which it treats is a stronger and surer one.—*The London Practitioner*, Jan. 1882.

HUTCHINSON, JONATHAN, F. R. S., F. R. C. S.,

Consulting Surgeon to the London Hospital.

Syphilis. In one 12mo. volume. *Preparing.* See *Series of Clinical Manuals*, page 3.

GROSS, SAMUEL W., A. M., M. D.,

Professor of the Principles of Surgery and of Clinical Surgery in the Jefferson Medical College.

A Practical Treatise on Impotence, Sterility, and Allied Disorders of the Male Sexual Organs. Second edition, thoroughly revised. In one very handsome octavo volume of 168 pages, with 16 illustrations. Cloth, $1.50.

The author of this monograph is a man of positive convictions and vigorous style. This is justified by his experience and by his study, which has gone hand in hand with his experience. In regard to the various organic and functional disorders of the male generative apparatus, he has had exceptional opportunities for observation, and his book shows that he has not neglected to compare his own views with those of other authors. The result is a work which can be safely recommended to both physicians and surgeons as a guide in the treatment of the disturbances it refers to. It is the best treatise on the subject with which we are acquainted.—*The Medical News*, Sept. 1, 1883.

This work will derive value from the high standing of its author, aside from the fact of its passing so rapidly into its second edition. This is, indeed, a book that every physician will be glad to place in his library, to be read with profit to himself, and with incalculable benefit to his patient. Besides the subjects embraced in the title, which are treated of in their various forms and degrees, spermatorrhœa and prostatorrhœa are also fully considered. The work is thoroughly practical in character, and will be especially useful to the general practitioner.—*Medical Record*, Aug. 18, 1883.

CULLERIER, A., & BUMSTEAD, F. J., M.D., LL.D.,

Surgeon to the Hôpital du Midi. *Late Professor of Venereal Diseases in the College of Physicians and Surgeons, New York.*

An Atlas of Venereal Diseases. Translated and edited by FREEMAN J. BUMSTEAD, M. D. In one imperial 4to. volume of 328 pages, double-columns, with 26 plates, containing about 150 figures, beautifully colored, many of them the size of life. Strongly bound in cloth, $17.00. A specimen of the plates and text sent by mail, on receipt of 25 cts.

HILL ON SYPHILIS AND LOCAL CONTAGIOUS DISORDERS. In one 8vo vol. of 479 p. Cloth, $3.25.

LEE'S LECTURES ON SYPHILIS AND SOME FORMS OF LOCAL DISEASE AFFECTING PRINCIPALLY THE ORGANS OF GENERATION. In one 8vo. vol. of 246 pages. Cloth, $2.25.

HYDE, J. NEVINS, A. M., M. D.,

Professor of Dermatology and Venereal Diseases in Rush Medical College, Chicago.

A Practical Treatise on Diseases of the Skin. For the use of Students and Practitioners. In one handsome octavo volume of 570 pages, with 66 beautiful and elaborate illustrations. Cloth, $4.25; leather, $5.25.

The author has given the student and practitioner a work admirably adapted to the wants of each. We can heartily commend the book as a valuable addition to our literature and a reliable guide to students and practitioners in their studies and practice.—*Am. Journ. of Med. Sci.*, July, 1883.

Especially to be praised are the practical suggestions as to what may be called the common-sense treatment of eczema. It is quite impossible to exaggerate the judiciousness with which the formulæ for the external treatment of eczema are selected, and what is of equal importance, the full and clear instructions for their use.—*London Medical Times and Gazette*, July 28, 1883.

The work of Dr. Hyde will be awarded a high position. The student of medicine will find it peculiarly adapted to his wants. Notwithstanding the extent of the subject to which it is devoted, yet it is limited to a single and not very large volume, without omitting a proper discussion of the topics. The conciseness of the volume, and the setting forth of only what can be held as facts will also make it acceptable to general practitioners. —*Cincinnati Medical News*, Feb. 1883.

The aim of the author has been to present to his readers a work not only expounding the most modern conceptions of his subject, but presenting what is of standard value. He has more especially devoted its pages to the treatment of disease, and by his detailed descriptions of therapeutic measures has adapted them to the needs of the physician in active practice. In dealing with these questions the author leaves nothing to the presumed knowledge of the reader, but enters thoroughly into the most minute description, so that one is not only told what should be done under given conditions but how to do it as well. It is therefore in the best sense "a practical treatise." That it is comprehensive, a glance at the index will show.—*Maryland Medical Journal*, July 7, 1883.

Professor Hyde has long been known as one of the most intelligent and enthusiastic representatives of dermatology in the west. His numerous contributions to the literature of this specialty have gained for him a favorable recognition as a careful, conscientious and original observer. The remarkable advances made in our knowledge of diseases of the skin, especially from the standpoint of pathological histology and improved methods of treatment, necessitate a revision of the older text-books at short intervals in order to bring them up to the standard demanded by the march of science. This last contribution of Dr. Hyde is an effort in this direction. He has attempted, as he informs us, the task of presenting in a condensed form the results of the latest observation and experience. A careful examinatiod of the work convinces us that he has accomplishen his task with painstaking fidelity and with a creditable result.—*Journal of Cutaneous and Venereal Diseases*, June, 1883.

FOX, T., M.D., F.R.C.P., and FOX, T.C., B.A., M.R.C.S.,

Physician to the Department for Skin Diseases, University College Hospital, London. — *Physician for Diseases of the Skin to the Westminster Hospital, London.*

An Epitome of Skin Diseases. With Formulæ. For Students and Practitioners. Third edition, revised and enlarged. In one very handsome 12mo. volume of 238 pages. Cloth, $1.25.

The third edition of this convenient handbook calls for notice owing to the revision and expansion which it has undergone. The arrangement of skin diseases in alphabetical order, which is the method of classification adopted in this work, becomes a positive advantage to the student. The book is one which we can strongly recommend, not only to students but also to practitioners who require a compendious summary of the present state of dermatology.—*British Medical Journal*, July 2, 1883.

We cordially recommend Fox's *Epitome* to those whose time is limited and who wish a handy manual to lie upon the table for instant reference. Its alphabetical arrangement is suited to this use, for all one has to know is the name of the disease, and here are its description and the appropriate treatment at hand and ready for instant application. The present edition has been very carefully revised and a number of new diseases are described, while most of the recent additions to dermal therapeutics find mention, and the formulary at the end of the book has been considerably augmented.—*The Medical News*, December, 1883.

MORRIS, MALCOLM, M. D.,

Joint Lecturer on Dermatology at St. Mary's Hospital Medical School, London.

Skin Diseases; Including their Definitions, Symptoms, Diagnosis, Prognosis, Morbid Anatomy and Treatment. A Manual for Students and Practitioners. In one 12mo. volume of 316 pages, with illustrations. Cloth, $1.75.

To physicians who would like to know something about skin diseases, so that when a patient presents himself for relief they can make a correct diagnosis and prescribe a rational treatment, we unhesitatingly recommend this little book of Dr. Morris. The affections of the skin are described in a terse, lucid manner, and their several characteristics so plainly set forth that diagnosis will be easy. The treatment in each case is such as the experience of the most eminent dermatologists advises.—*Cincinnati Medical News*, April, 1880.

This is emphatically a learner's book; for we can safely say, that in the whole range of medical literature there is no book of a like scope which for clearness of expression and methodical arrangement is better adapted to promote a rational conception of dermatology—a branch confessedly difficult and perplexing to the beginner.—*St. Louis Courier of Medicine*, April, 1880.

The writer has certainly given in a small compass a large amount of well-compiled information, and his little book compares favorably with any other which has emanated from England, while in many points he has emancipated himself from the stubbornly adhered to errors of others of his countrymen. There is certainly excellent material in the book which will well repay perusal.—*Boston Med. and Surg. Journ.*, March, 1880.

WILSON, ERASMUS, F. R. S.

The Student's Book of Cutaneous Medicine and Diseases of the Skin. In one handsome small octavo volume of 535 pages. Cloth, $3.50.

HILLIER, THOMAS, M. D.,

Physician to the Skin Department of University College, London.

Handbook of Skin Diseases; for Students and Practitioners. Second American edition. In one 12mo. volume of 353 pages, with plates. Cloth, $2.25.

AN AMERICAN SYSTEM OF GYNÆCOLOGY.

A System of Gynæcology, in Treatises by Various Authors. Edited by MATTHEW D. MANN, M. D., Professor of Obstetrics and Gynæcology in the University of Buffalo, N. Y. In two handsome octavo volumes, richly illustrated. *In active preparation.*

LIST OF CONTRIBUTORS.

WILLIAM H. BAKER, M. D.,
FORDYCE BARKER, M. D.,
ROBERT BATTEY, M. D.,
SAMUEL C. BUSEY, M. D.,
HENRY F. CAMPBELL, M. D.,
HENRY C. COE, M. D.,
E. C. DUDLEY, M. D.,
GEORGE J. ENGELMANN, M. D.,
HENRY F. GARRIGUES, M. D.,
WILLIAM GOODELL, M. D.,
EGBERT H. GRANDIN, M. D.,
SAMUEL W. GROSS, M. D.,
JAMES B. HUNTER, M. D.,
A. REEVES JACKSON, M. D.,
EDWARD W. JENKS, M. D.,
WILLIAM T. LUSK, M. D.,
MATTHEW D. MANN, M. D.,
ROBERT B. MAURY, M. D.,
PAUL F. MUNDÉ, M. D.,
C. D. PALMER, M. D.,
WILLIAM M. POLK, M. D.,
THADDEUS A. REAMY, M. D.,
A. D. ROCKWELL, M. D.,
ALEX. J. C. SKENE, M. D.,
R. STANSBURY SUTTON, A. M., M. D.,
T. GAILLARD THOMAS, M. D.,
ELI VAN DE WALKER, M. D.,
W. GILL WYLIE, M. D.

THOMAS, T. GAILLARD, M. D.,

Professor of Diseases of Women in the College of Physicians and Surgeons, N. Y.

A Practical Treatise on the Diseases of Women. Fifth edition, thoroughly revised and rewritten. In one large and handsome octavo volume of 810 pages, with 266 illustrations. Cloth, $5.00; leather, $6.00; very handsome half Russia, raised bands, $6.50.

The words which follow "fifth edition" are in this case no mere formal announcement. The alterations and additions which have been made are both numerous and important. The attraction and the permanent character of this book lie in the clearness and truth of the clinical descriptions of diseases; the fertility of the author in therapeutic resources and the fulness with which the details of treatment are described; the definite character of the teaching; and last, but not least, the evident candor which pervades it. We would also particularize the fulness with which the history of the subject is gone into, which makes the book additionally interesting and gives it value as a work of reference.—*London Medical Times and Gazette*, July 30, 1881.

The determination of the author to keep his book foremost in the rank of works on gynæcology is most gratifying. Recognizing the fact that this can only be accomplished by frequent and thorough revision, he has spared no pains to make the present edition more desirable even than the previous one. As a book of reference for the busy practitioner it is unequalled.—*Boston Medical any Surgical Journal*, April 7, 1880.

It has been enlarged and carefully revised. It is a condensed encyclopædia of gynæcological medicine. The style of arrangement, the masterly manner in which each subject is treated, and the honest convictions derived from probably the largest clinical experience in that specialty of any in this country, all serve to commend it in the highest terms to the practitioner.—*Nashville Jour. of Med. and Surg.*, Jan. 1881.

That the previous editions of the treatise of Dr. Thomas were thought worthy of translation into German, French, Italian and Spanish, is enough to give it the stamp of genuine merit. At home it has made its way into the library of every obstetrician and gynæcologist as a safe guide to practice. No small number of additions have been made to the present edition to make it correspond to recent improvements in treatment.—*Pacific Medical and Surgical Journal*, Jan. 1881.

EDIS, ARTHUR W., M. D., Lond., F. R. C. P., M. R. C. S.,

Assist. Obstetric Physician to Middlesex Hospital, late Physician to British Lying-in Hospital.

The Diseases of Women. Including their Pathology, Causation, Symptoms, Diagnosis and Treatment. A Manual for Students and Practitioners. In one handsome octavo volume of 576 pages, with 148 illustrations. Cloth, $3.00; leather, $4.00.

It is a pleasure to read a book so thoroughly good as this one. The special qualities which are conspicuous are thoroughness in covering the whole ground, clearness of description and conciseness of statement. Another marked feature of the book is the attention paid to the details of many minor surgical operations and procedures, as, for instance, the use of tents, application of leeches, and use of hot water injections. These are among the more common methods of treatment, and yet very little is said about them in many of the text-books. The book is one to be warmly recommended especially to students and general practitioners, who need a concise but complete *résumé* of the whole subject. Specialists, too, will find many useful hints in its pages.—*Boston Med. and Surg. Journ.*, March 2, 1882.

The greatest pains have been taken with the sections relating to treatment. A liberal selection of remedies is given for each morbid condition, the strength, mode of application and other details being fully explained. The descriptions of gynæcological manipulations and operations are full, clear and practical. Much care has also been bestowed on the parts of the book which deal with diagnosis—we note especially the pages dealing with the differentiation, one from another, of the different kinds of abdominal tumors. The practitioner will therefore find in this book the kind of knowledge he most needs in his daily work, and he will be pleased with the clearness and fulness of the information there given.—*The Practitioner*, Feb. 1882.

BARNES, ROBERT, M. D., F. R. C. P.,

Obstetric Physician to St. Thomas' Hospital, London, etc.

A Clinical Exposition of the Medical and Surgical Diseases of Women. In one handsome octavo volume, with numerous illustrations. New edition. *Preparing.*

WEST, CHARLES, M. D.

Lectures on the Diseases of Women. Third American from the third London edition. In one octavo volume of 543 pages. Cloth, $3.75; leather, $4.75.

EMMET, THOMAS ADDIS, M. D., LL. D.,

Surgeon to the Woman's Hospital, New York, etc.

The Principles and Practice of Gynæcology; For the use of Students and Practitioners of Medicine. New (third) edition, thoroughly revised. In one large and very handsome octavo volume of 880 pages, with 150 illustrations. Cloth, $5; leather, $6. (*Just ready.*)

We are in doubt whether to congratulate the author more than the profession upon the appearance of the third edition of this well-known work. Embodying, as it does, the life-long experience of one who has conspicuously distinguished himself as a bold and successful operator, and who has devoted so much attention to the specialty, we feel sure the profession will not fail to appreciate the privilege thus offered them of perusing the views and practice of the author. His earnestness of purpose and conscientiousness are manifest. He gives not only his individual experience but endeavors to represent the actual state of gynæcological science and art.—*British Medical Journal*, May 16, 1885.

No jot or tittle of the high praise bestowed upon the first edition is abated. It is still a book of marked personality, one based upon large clinical experience, containing large and valuable additions to our knowledge, evidently written not only with honesty of purpose, but with a conscientious sense of responsibility, and a book that is at once a credit to its author and to American medical literature. We repeat that it is a book to be studied, and one that is indispensable to every practitioner giving any attention to gynæcology.—*American Journal of the Medical Sciences*, April, 1885.

The time has passed when Emmet's *Gynæcology* was to be regarded as a book for a single country or for a single generation. It has always been his aim to popularize gynæcology, to bring it within easy reach of the general practitioner. The originality of the ideas, aside from the perfect confidence which we feel in the author's statements, compels our admiration and respect. We may well take an honest pride in Dr. Emmet's work and feel that his book can hold its own against the criticism of two continents. It represents all that is most earnest and most thoughtful in American gynæcology. Emmet's work will continue to reflect the individuality, the sterling integrity and the kindly heart of its honored author long after smaller books have been forgotten.—*American Journal of Obstetrics*, May, 1885.

Any work on gynæcology by Emmet must always have especial interest and value. He has for many years been an exceedingly busy practitioner in this department. Few men have had his experience and opportunities. As a guide either for the general practitioner or specialist, it is second to none other. No one can read Emmet without pleasure, instruction and profit. —*Cincinnati Lancet and Clinic*, Jan 31, 1885.

DUNCAN, J. MATTHEWS, M.D., LL. D., F. R. S. E., etc.

Clinical Lectures on the Diseases of Women; Delivered in Saint Bartholomew's Hospital. In one handsome octavo volume of 175 pages. Cloth, $1.50.

They are in every way worthy of their author; indeed, we look upon them as among the most valuable of his contributions. They are all upon matters of great interest to the general practitioner. Some of them deal with subjects that are not, as a rule, adequately handled in the text-books; others of them, while bearing upon topics that are usually treated of at length in such works, yet bear such a stamp of individuality that, if widely read, as they certainly deserve to be, they cannot fail to exert a wholesome restraint upon the undue eagerness with which many young physicians seem bent upon following the wild teachings which so infest the gynæcology of the present day.—*N. Y. Medical Journal*, March, 1880.

MAY, CHARLES H., M. D.

Late House Surgeon to Mount Sinai Hospital, New York.

A Manual of the Diseases of Women. Containing a concise and systematic exposition of theory and practice. In one 12mo. volume of about 350 pages. *In press.*

HODGE, HUGH L., M. D.,

Emeritus Professor of Obstetrics, etc., in the University of Pennsylvania.

On Diseases Peculiar to Women; Including Displacements of the Uterus. Second edition, revised and enlarged. In one beautifully printed octavo volume of 519 pages, with original illustrations. Cloth, $4.50.

By the Same Author.

The Principles and Practice of Obstetrics. Illustrated with large lithographic plates containing 159 figures from original photographs, and with numerous woodcuts. In one large quarto volume of 542 double-columned pages. Strongly bound in cloth, $14.00.

* * * Specimens of the plates and letter-press will be forwarded to any address, free by mail, on receipt of six cents in postage stamps.

RAMSBOTHAM, FRANCIS H., M. D.

The Principles and Practice of Obstetric Medicine and Surgery; In reference to the Process of Parturition. A new and enlarged edition, thoroughly revised by the Author. With additions by W. V. KEATING, M. D., Professor of Obstetrics, etc., in the Jefferson Medical College of Philadelphia. In one large and handsome imperial octavo volume of 640 pages, with 64 full-page plates and 43 woodcuts in the text, containing in all nearly 200 beautiful figures. Strongly bound in leather, with raised bands, $7.

ASHWELL'S PRACTICAL TREATISE ON THE DISEASES PECULIAR TO WOMEN. Third American from the third and revised London edition. In one 8vo. vol., pp. 520. Cloth, $3.50.

CHURCHILL ON THE PUERPERAL FEVER AND OTHER DISEASES PECULIAR TO WOMEN. In one 8vo. vol. of 464 pages. Cloth, $2.50.

MEIGS ON THE NATURE, SIGNS AND TREATMENT OF CHILDBED FEVER. In one 8vo. volume of 346 pages. Cloth, $2.00.

PLAYFAIR, W. S., M. D., F. R. C. P.,

Professor of Obstetric Medicine in King's College, London, etc.

A Treatise on the Science and Practice of Midwifery. New (fourth) American, from the fifth English edition. Edited, with additions, by ROBERT P. HARRIS, M. D. In one handsome octavo volume of 654 pages, with 3 plates and 201 engravings Cloth, $4; leather, $5; half Russia, $5.50. *Just ready.*

This excellent work needs no commendation. For many years it has maintained a deservedly high reputation among teachers as a text book, and in the profession as a guide to the practical experiences which attend the obstetrician. The present edition, under the supervision of Dr. Harris, has been carefully revised, and many portions rewritten, and the whole work has been adapted to the wants and circumstances of this continent.—*Buffalo Medical and Surgical Journal*, Aug. 1885.

In the short time that this excellent and highly esteemed work has been before the profession it has reached a fourth edition in this country and a fifth one in England. This fact alone speaks in high praise of it, and it seems to us that scarcely more need be said of it in the way of endorsement of its value. As a text book for students and for the uses of the general practitioner there is no work on obstetrics superior to the work of Dr. Playfair. Its teachings are practical, written in plain language, and afford a correct understanding of the art of midwifery. No one can be disappointed in it.—*Cincinnati Medical News*, June, 1885.

BARNES, ROBERT, M. D., and FANCOURT, M. D.,

Phys. to the General Lying-in Hosp., Lond. *Obstetric Phys. to St. Thomas' Hosp., Lond.*

A System of Obstetric Medicine and Surgery, Theoretical and Clinical. For the Student and the Practitioner. The Section on Embryology contributed by Prof. Milnes Marshall. In one handsome octavo volume of about 1000 pages, profusely illustrated. Cloth, $5; leather, $6. *In a few days.*

BARKER, FORDYCE, A. M., M. D., LL. D. Edin.,

Clinical Professor of Midwifery and the Diseases of Women in the Bellevue Hospital Medical College, New York, Honorary Fellow of the Obstetrical Societies of London and Edinburgh, etc., etc.

Obstetrical and Clinical Essays. In one handsome 12mo. volume of about 300 pages. *Preparing.*

KING, A. F. A., M. D.,

Professor of Obstetrics and Diseases of Women in the Medical Department of the Columbian University, Washington, D. C., and in the University of Vermont, etc.

A Manual of Obstetrics. Second edition. In one very handsome 12mo. volume of 331 pages, with 59 illustrations. Cloth, $2.00.

It must be acknowledged that this is just what it pretends to be—a sound guide, a portable epitome, a work in which only indispensable matter has been presented, leaving out all padding and chaff, and one in which the student will find pure wheat or condensed nutriment.—*New Orleans Medical and Surgical Journal*, May, 1884.

In a series of short paragraphs and by a condensed style of composition, the writer has presented a great deal of what it is well that every obstetrician should know and be ready to practice or prescribe. The fact that the demand for the volume has been such as to exhaust the first edition in a little over a year and a half speaks well for its popularity.—*American Journal of the Medical Sciences*, April, 1884.

LANDIS, HENRY G., A. M., M. D.,

Professor of Obstetrics and the Diseases of Women in Starling Medical College, Columbus, O.

The Management of Labor. In one handsome 12mo. volume of about 300 pages, with 30 illustrations. *Shortly.*

BARNES, FANCOURT, M. D.,

Obstetric Physician to St. Thomas' Hospital, London.

A Manual of Midwifery for Midwives and Medical Students. In one royal 12mo. volume of 197 pages, with 50 illustrations. Cloth, $1.25.

PARVIN, THEOPHILUS, M. D., LL. D.,

Professor of Obstetrics and the Diseases of Women and Children in the Jefferson Medical College.

A Treatise on Midwifery. In one very handsome octavo volume of about 550 pages, with numerous illustrations. *In press.*

PARRY, JOHN S., M. D.,

Obstetrician to the Philadelphia Hospital, Vice-President of the Obstet. Society of Philadelphia.

Extra-Uterine Pregnancy: Its Clinical History, Diagnosis, Prognosis and Treatment. In one handsome octavo volume of 272 pages. Cloth, $2.50.

TANNER, THOMAS HAWKES, M. D.

On the Signs and Diseases of Pregnancy. First American from the second English edition. Octavo, 490 pages, with 4 colored plates and 16 woodcuts. Cloth, $4.25.

WINCKEL, F.

A Complete Treatise on the Pathology and Treatment of Childbed, For Students and Practitioners. Translated, with the consent of the Author, from the second German edition, by J. R. CHADWICK, M. D. Octavo 484 pages. Cloth, $4.00.

LEISHMAN, WILLIAM, M. D.,

Regius Professor of Midwifery in the University of Glasgow, etc.

A System of Midwifery, Including the Diseases of Pregnancy and the Puerperal State. Third American edition, revised by the Author, with additions by JOHN S. PARRY, M. D., Obstetrician to the Philadelphia Hospital, etc. In one large and very handsome octavo volume of 740 pages, with 205 illustrations. Cloth, $4.50; leather, $5.50; very handsome half Russia, raised bands, $6.00.

The author is broad in his teachings, and discusses briefly the comparative anatomy of the pelvis and the mobility of the pelvic articulations. The second chapter is devoted especially to the study of the pelvis, while in the third the female organs of generation are introduced. The structure and development of the ovum are admirably described. Then follow chapters upon the various subjects embraced in the study of midwifery. The descriptions throughout the work are plain and pleasing. It is sufficient to state that in this, the last edition of this well-known work, every recent advancement in this field has been brought forward.—*Physician and Surgeon*, Jan. 1880.

We gladly welcome the new edition of this excellent text-book of midwifery. The former editions have been most favorably received by the profession on both sides of the Atlantic. In the preparation of the present edition the author has made such alterations as the progress of obstetrical science seems to require, and we cannot but admire the ability with which the task has been performed. We consider it an admirable text-book for students during their attendance upon lectures, and have great pleasure in recommending it. As an exponent of the midwifery of the present day it has no superior in the English language.—*Canada Lancet*, Jan. 1880.

To the American student the work before us must prove admirably adapted. Complete in all its parts, essentially modern in its teachings, and with demonstrations noted for clearness and precision, it will gain in favor and be recognized as a work of standard merit. The work cannot fail to be popular and is cordially recommended.—*N. O. Med. and Surg. Journ.*, March, 1880.

SMITH, J. LEWIS, M. D.,

Clinical Professor of Diseases of Children in the Bellevue Hospital Medical College, N. Y.

A Complete Practical Treatise on the Diseases of Children. Fifth edition, thoroughly revised and rewritten. In one handsome octavo volume of 836 pages, with illustrations. Cloth, $4.50; leather, $5.50; very handsome half Russia, raised bands, $6.

This is one of the best books on the subject with which we have met and one that has given us satisfaction on every occasion on which we have consulted it, either as to diagnosis or treatment. It is now in its fifth edition and in its present form is a very adequate representation of the subject it treats of as at present understood. The important subject of infant hygiene is fully dealt with in the early portion of the book. The great bulk of the work is appropriately devoted to the diseases of infancy and childhood. We would recommend any one in need of information on the subject to procure the work and form his own opinion on it, which we venture to say will be a favorable one.—*Dublin Journal of Medical Science*, March, 1883.

There is no book published on the subjects of which this one treats that is its equal in value to the physician. While he has said just enough to impart the information desired by general practitioners on such questions as etiology, pathology, prognosis, etc., he has devoted more attention to the diagnosis and treatment of the ailments which he so accurately describes; and such information is exactly what is wanted by the vast majority of "family physicians."—*Va. Med. Monthly*, Feb. 1882.

KEATING, JOHN M., M. D.,

Lecturer on the Diseases of Children at the University of Pennsylvania, etc.

The Mother's Guide in the Management and Feeding of Infants. In one handsome 12mo. volume of 118 pages. Cloth, $1.00.

Works like this one will aid the physician immensely, for it saves the time he is constantly giving his patients in instructing them on the subjects here dwelt upon so thoroughly and practically. Dr. Keating has written a practical book, has carefully avoided unnecessary repetition, and successfully instructed the mother in such details of the treatment of her child as devolve upon her. He has studiously omitted giving prescriptions, and instructs the mother when to call upon the doctor, as his duties are totally distinct from hers. —*American Journal of Obstetrics*, October, 1881.

Dr. Keating has kept clear of the common fault of works of this sort, viz., mixing the duties of the mother with those proper to the doctor. There is the ring of common sense in the remarks about the employment of a wet-nurse, about the proper food for a nursing mother, about the tonic effects of a bath, about the perambulator *versus* the nurses, arms, and on many other subjects concerning which the critic might say, "surely this is obvious," but which experience teaches us are exactly the things needed to be insisted upon, with the rich as well as the poor.—*London Lancet*, January, 28 1882.

A book small in size, written in pleasant style, in language which can be readily understood by any mother, and eminently practical and safe; in fact a book for which we have been waiting a long time, and which we can most heartily recommend to mothers as *the* book on this subject.—*New York Medical Journal and Obstetrical Review*, Feb. 1882.

OWEN, EDMUND, M. B., F. R. C. S.,

Surgeon to the Children's Hospital, Great Ormond St., London.

Surgical Diseases of Children. In one 12mo. volume. *Preparing.* See *Series of Clinical Manuals*, page 3.

WEST, CHARLES, M. D.,

Physician to the Hospital for Sick Children, London, etc.

Lectures on the Diseases of Infancy and Childhood. Fifth American from 6th English edition. In one octavo volume of 686 pages. Cloth, $4.50; leather, $5.50.

By the Same Author.

On Some Disorders of the Nervous System in Childhood. In one small 12mo. volume of 127 pages. Cloth, $1.00.

CONDIE'S PRACTICAL TREATISE ON THE DISEASES OF CHILDREN. Sixth edition, revised and augmented. In one octavo volume of 779 pages. Cloth, $5.25; leather, $6.25.

TIDY, CHARLES MEYMOTT, M. B., F. C. S.,

Professor of Chemistry and of Forensic Medicine and Public Health at the London Hospital, etc.

Legal Medicine. VOLUME II. Legitimacy and Paternity, Pregnancy, Abortion, Rape, Indecent Exposure, Sodomy, Bestiality, Live Birth, Infanticide, Asphyxia, Drowning, Hanging, Strangulation, Suffocation. Making a very handsome imperial octavo volume of 529 pages. Cloth, $6.00; leather, $7.00.

VOLUME I. Containing 664 imperial octavo pages, with two beautiful colored plates. Cloth, $6.00; leather, $7.00.

The satisfaction expressed with the first portion of this work is in no wise lessened by a perusal of the second volume. We find it characterized by the same fulness of detail and clearness of expression which we had occasion so highly to commend in our former notice, and which render it so valuable to the medical jurist. The copious tables of cases appended to each division of the subject, must have cost the author a prodigious amount of labor and research, but they constitute one of the most valuable features of the book, especially for reference in medico-legal trials.—*American Journal of the Medical Sciences*, April, 1884.

TAYLOR, ALFRED S., M. D.,

Lecturer on Medical Jurisprudence and Chemistry in Guy's Hospital, London.

A Manual of Medical Jurisprudence. Eighth American from the tenth London edition, thoroughly revised and rewritten. Edited by JOHN J. REESE, M. D., Professor of Medical Jurisprudence and Toxicology in the University of Pennsylvania. In one large octavo volume of 937 pages, with 70 illustrations. Cloth, $5.00; leather, $6.00; half Russia, raised bands, $6.50.

The American editions of this standard manual have for a long time laid claim to the attention of the profession in this country; and the eighth comes before us as embodying the latest thoughts and emendations of Dr. Taylor upon the subject to which he devoted his life with an assiduity and success which made him *facile princeps* among English writers on medical jurisprudence. Both the author and the book have made a mark too deep to be affected by criticism, whether it be censure or praise. In this case, however, we should only have to seek for laudatory terms.—*American Journal of the Medical Sciences*, Jan. 1881.

This celebrated work has been the standard authority in its department for thirty-seven years, both in England and America, in both the professions which it concerns, and it is improbable that it will be superseded in many years. The work is simply indispensable to every physician, and nearly so to every liberally-educated lawyer, and we heartily commend the present edition to both professions.—*Albany Law Journal*, March 26, 1881.

By the Same Author.

The Principles and Practice of Medical Jurisprudence. Third edition. In two handsome octavo volumes, containing 1416 pages, with 188 illustrations. Cloth, $10; leather, $12. *Just ready.*

For years Dr. Taylor was the highest authority in England upon the subject to which he gave especial attention. His experience was vast, his judgment excellent, and his skill beyond cavil. It is therefore well that the work of one who, as Dr. Stevenson says, had an "enormous grasp of all matters connected with the subject," should be brought up to the present day and continued in its authoritative position. To accomplish this result Dr. Stevenson has subjected it to most careful editing, bringing it well up to the times.—*American Journal of the Medical Sciences*, Jan. 1884.

By the Same Author.

Poisons in Relation to Medical Jurisprudence and Medicine. Third American, from the third and revised English edition. In one large octavo volume of 788 pages. Cloth, $5.50; leather, $6.50.

PEPPER, AUGUSTUS J., M. S., M. B., F. R. C. S.,

Examiner in Forensic Medicine at the University of London.

Forensic Medicine. In one pocket-size 12mo. volume. *Preparing.* See *Students' Series of Manuals*, page 3.

LEA, HENRY C.

Superstition and Force: Essays on The Wager of Law, The Wager of Battle, The Ordeal and Torture. Third revised and enlarged edition. In one handsome royal 12mo. volume of 552 pages. Cloth, $2.50.

This valuable work is in reality a history of civilization as interpreted by the progress of jurisprudence. . . In "Superstition and Force" we have a philosophic survey of the long period intervening between primitive barbarity and civilized enlightenment. There is not a chapter in the work that should not be most carefully studied; and however well versed the reader may be in the science of jurisprudence, he will find much in Mr. Lea's volume of which he was previously ignorant. The book is a valuable addition to the literature of social science.—*Westminster Review*, Jan. 1880.

By the Same Author.

Studies in Church History. The Rise of the Temporal Power—Benefit of Clergy—Excommunication. New edition. In one very handsome royal octavo volume of 605 pages. Cloth, $2.50. *Just ready.*

The author is pre-eminently a scholar. He takes up every topic allied with the leading theme, and traces it out to the minutest detail with a wealth of knowledge and impartiality of treatment that compel admiration. The amount of information compressed into the book is extraordinary. In no other single volume is the development of the primitive church traced with so much clearness, and with so definite a perception of complex or conflicting sources. The fifty pages on the growth of the papacy, for instance, are admirable for conciseness and freedom from prejudice.—*Boston Traveller*, May 3, 1883.

Books marked * are also bound in half Russia.

LEA BROTHERS & CO., Philadelphia.